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*Public hearings*

**CANADIAN** *Petroleum* **ASSOCIATION**

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Submission to the Environment Conservati  
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Submission to

*Alberta*

ENVIRONMENT CONSERVATION AUTHORITY

*[briefs]*

on

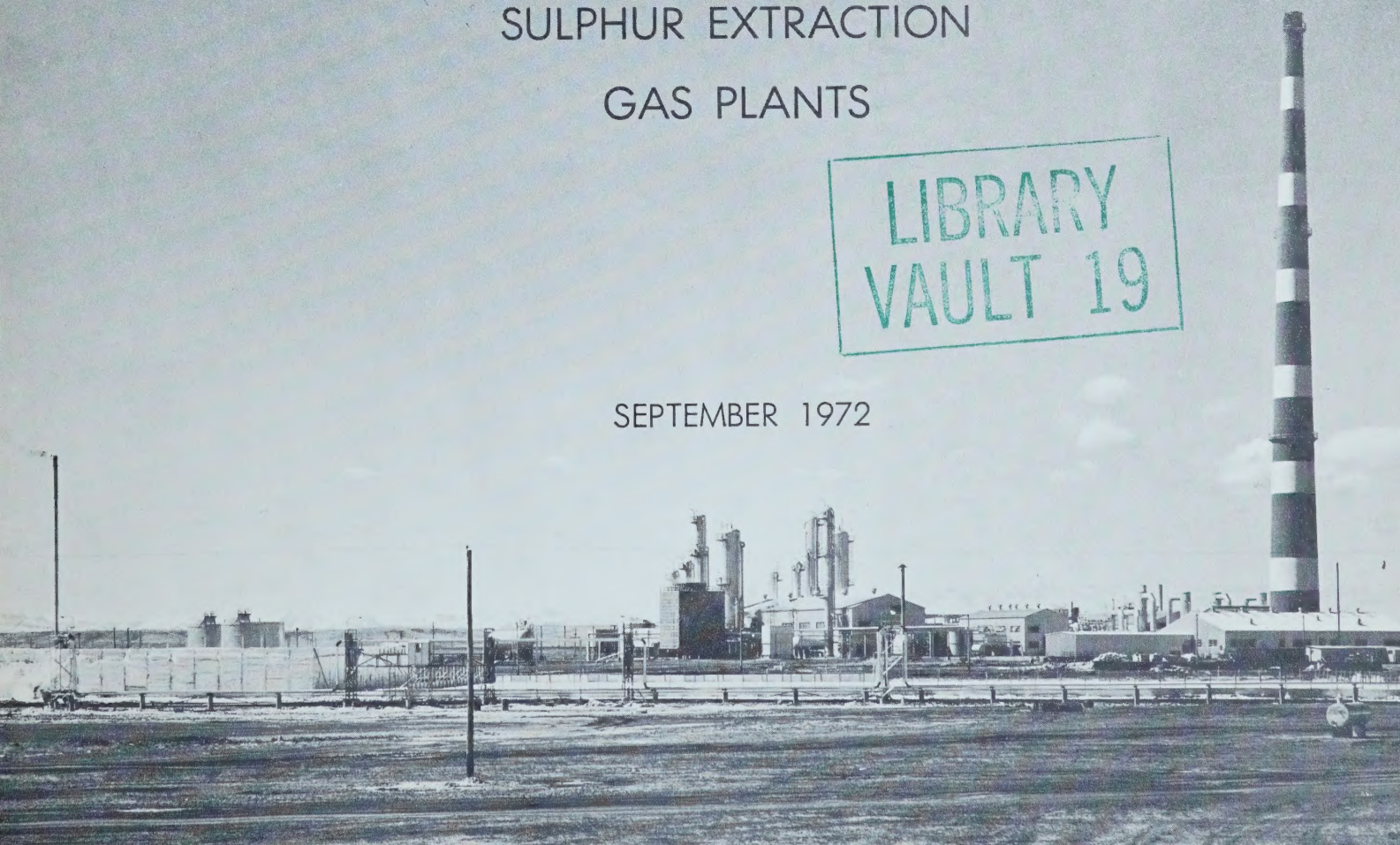
*Public hearings on the*  
ENVIRONMENTAL EFFECTS

OF THE OPERATION OF  
SULPHUR EXTRACTION

GAS PLANTS

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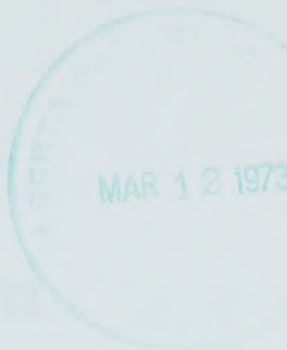
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CANADIAN PETROLEUM ASSOCIATION

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ENVIRONMENT CONSERVATION AUTHORITY



Introduction & Policy Statement

The series of papers submitted to the Environmental Effects of the Operation of Sulphur Extraction Gas Plants in Alberta was prepared by the Canadian Petroleum Association.

CANADIAN PETROLEUM ASSOCIATION

Conservation Authority, 1111 14th Street, N.W., Ottawa, Ontario, K1P 6K6, Canada.

The purpose of this submission is to provide information to the Conservation Authority regarding the environmental effects of the operation of sulphur extraction gas plants in Alberta.

Submission to the

ENVIRONMENT CONSERVATION AUTHORITY

The following information was prepared by the Canadian Petroleum Association for the Environmental Effects of the Operation of Sulphur Extraction Gas Plants in Alberta. It is intended to provide information to the Conservation Authority regarding the environmental effects of the operation of sulphur extraction gas plants in Alberta.

The Environmental Effects

Of the Operation of Sulphur

Extraction Gas Plants in Alberta

Technical  
ships  
their  
est.

It is the policy of the Canadian Petroleum Association to provide information to the Conservation Authority regarding the environmental effects of the operation of sulphur extraction gas plants in Alberta.

More specifically, the series of papers submitted to the Conservation Authority was prepared by the Canadian Petroleum Association for the Environmental Effects of the Operation of Sulphur Extraction Gas Plants in Alberta. It is intended to provide information to the Conservation Authority regarding the environmental effects of the operation of sulphur extraction gas plants in Alberta.

September 29, 1972





CANADIAN PETROLEUM ASSOCIATION

BRIEF TO

ENVIRONMENT CONSERVATION AUTHORITY

Introduction & Policy Statement

The series of public hearings on the Environmental Effects of the Operation of Sulphur Extraction Gas Plants in Alberta was announced by the chairman of the Environment Conservation Authority - Dr. W. R. Trost on July 14, 1972. The prospectus for public hearings, which was included in the announcement stated in part:

The Authority hopes that some briefs will be able to provide first hand or specialized information on particular aspects of the subject about which general knowledge is deficient, or where misconceptions might be considered to exist.

Factual information or data on cause/effect relationships connected with the operation of gas plants and their transmission lines, would be of particular interest.

It is in response to these two general requests that the members of the Canadian Petroleum Association has directed the major portion of their brief.

More specifically, our brief considers each of the sixteen points, which the two consultants for the Environment Conservation Authority, Dr. William MacDonald and Dr. Roger Klemn, accepted as their terms of reference, in preparing their "resume of the sour gas industry and its



LEGISLATIVE ASSEMBLY OF ALBERTA

OFFICE OF THE CLERK

LEGISLATIVE ASSEMBLY OF ALBERTA

Introduction of Bill

The House of Commons has the honour to acknowledge the receipt of the Bill from the Government of Alberta, dated the 1st day of June, 1954.

The Bill is entitled "The Conservation Act" and is intended to provide for the conservation of the natural resources of the Province of Alberta.

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The Bill is intended to provide for the conservation of the natural resources of the Province of Alberta.

It is the intention of the Government of Alberta to introduce this Bill into the Legislative Assembly of Alberta.

More specifically, the Bill is intended to provide for the conservation of the natural resources of the Province of Alberta.



attendant impact upon the province of Alberta". The authors (MacDonald and Klemn) have admirably accomplished their stated purpose viz. - "to outline the present situation in Alberta concerning sulphur extraction plants and to describe the present technology employed in sulphur extraction".

Certainly, in light of the short two and one-half months allotted the authors to gather the information on such a broad subject they have performed a creditable job.

While one may well question, in an environmental effects investigation, the relevancy of such matters as:

- (i) foreign ownerships of both plants' operating and construction companies, or
- (ii) the few personnel directly employed in the highly automated process industry versus the older and highly labor intensive manufacturing industries,

the CPA Committee has addressed itself to the Environmental and Technical aspects of the Status Report.

The Canadian Petroleum Association represents some 191 oil and gas exploration and producing companies in the province of Alberta.

The association's Environmental Conservation Policy clearly states our desire to participate in public hearings such as this, in order that we may assist the Environment Conservation Authority as they enquire into all affects on the environment of the operation of sulphur extraction plants and review all legislation pertaining thereto.







ENVIRONMENTAL CONSERVATION

Statement of Policy

by

CANADIAN PETROLEUM ASSOCIATION

1. The Canadian Petroleum Association fully supports and encourages efforts to prevent pollution and conserve Canada's environmental resources.
2. The Association believes the responsibility for protecting our environmental resources should be shared by individual citizens, business and industry and municipal, provincial and federal governments.
3. The Association supports the efforts of Federal and Provincial governments to continually reappraise standards for conservation of air, water and soil resources. The Association believes that the federal government can provide general guidelines and minimum standards, but that the provincial governments should establish environmental regulations and standards which are applicable to specific local circumstances within that provincial government's jurisdiction.
4. The Association endorses intensive, cooperative government, industry and university study of environmental conservation. The Association believes that thorough study of all scientific, economic and social factors is the only sound and responsible basis for environmental regulations and standards.

Approved by the Board of Governors, January 30, 1966.





5. The Association pledges continued cooperation with all levels of government to seek practical standards to assure effective and economic utilization and conservation of our environmental resources. The Association welcomes any opportunity to review proposed legislation and prepare constructive comments for consideration by governmental authorities.
6. The Association is pleased to act on behalf of the Canadian exploration, development, production and pipeline segments of the petroleum industry in support of this policy.





## SUMMARY

In the preparation of this brief the Canadian Petroleum Association engaged the services of five consultants to study and report on the environmental impact of Sulphur Recovery Plants in the province of Alberta. The results of the consultant's investigations, combined with those of an "in-house" study by a special task force of the CPA's Environmental Conservation Committee, constitute our submission.

The initial section of the report considers briefly the "Industry", in terms of its history and economic benefits to the province, and somewhat more extensively the industrial practices as they relate to the welfare of operating personnel and to the protection of the environment beyond the plant boundaries.

The brief next considers the consultant's reports, which include extensive literature searches as well as personal investigations of the effects of sulphur dioxide on vegetation, animal life and human welfare. These data were subsequently used to assess Air Quality Standards and the Legislation pertaining thereto in the ensuing sections of the brief. This assessment indicated that the legislation governing the Sulphur Recovery Industry is presently adequate to protect the environment.

An intensive evaluation of the methods employed in stack design for various conditions illustrated that the present methods constitute a sound design basis.

The effectiveness of the incinerator stack is continuously monitored to ensure that the established air quality stand-





ards are being achieved. Outlined in the brief are several promising new techniques for rapid assessment of environmental reaction, along with methods to assist in differentiating between natural and induced vegetation stresses.

Finally, the brief presents some indication of the extensive research programs both within the industry and by industry sponsored research groups to further technological advances.





## CONCLUSIONS

1. Natural gas processing plants with sulphur extraction facilities are a vital segment of the primary resource industry of Alberta. 62 such plants exist in the province and it is estimated that the investment for their construction totals over \$600 million. These plants are responsible for an annual direct operating monetary flow of about \$50 MM for payroll, supplies, municipal taxes, etc. In addition to their provincial impact, such plants are also important on the national scene. They provide other industries with reliable and economic supplies of fuel and petroleum products, and they purchase large quantities of manufactured products of all types.
2. The industry maintains up-to-date awareness of the latest technology as it concerns the conservation of the environment, and will continue to apply this technology to plant operations.
3. The sulphur industry is operating under strict regulations and supervision by both sulphur plant operators and the government. Emission monitoring and control procedures are effective in assuring satisfactory ground level concentrations.
4. The present Alberta Ambient Air Quality Standards with respect to sulphur dioxide and hydrogen sulphide are comparable to the national, and most international standards, which are designed to protect vegetation, animal life and human well-being.





5. Present methods of calculating ground level concentration of  $\text{SO}_2$  from sulphur stack emissions are conservative and the record shows them to be adequate for equipment design purposes.
6. The safety performance records established in this potentially hazardous industry illustrates the results of careful design coupled with responsible operating practices.





## RECOMMENDATIONS

1. The Canadian Petroleum Association recommends retention of the present Alberta Ambient Air Quality Standards for  $\text{SO}_2$  and  $\text{H}_2\text{S}$ .
2. The Department of the Environment, in conjunction with industry, should be responsible for developing Ambient Air Quality Standards in accordance with scientifically established criteria. The Energy Resources Conservation Board should be responsible for the enforcement of air quality within these standards for the industry without resorting to additional restrictive standards.
3. Measured ground level concentrations of sulphur compounds should be the sole consideration in limiting emissions of waste gases. Air Quality Standards should be maintained through ambient air monitoring and not through restrictions on the concentration of sulphur dioxide in the stack or through the specification of sulphur recovery efficiencies.
4. Present methods employed by the Energy Resources Conservation Board for predicting ground level concentrations of  $\text{SO}_2$  for specific stack conditions are adequate for relatively flat terrain and normal meteorological conditions and should be retained. More complex analyses of ground level concentration is recommended where unique topographical or meteorological features exist.





## I THE INDUSTRY

- A. History
- B. Future Trends
- C. Economics
  - 1. Plant Economics
  - 2. Economic Benefits to Alberta
- D. Industry Safe Operating Practises
  - 1. General
  - 2. Drilling
  - 3. Producing Operations
  - 4. Pipelines
  - 5. Plant Operations
    - a. General
    - b. Explosions and Fire
    - c.  $\text{H}_2\text{S}$  Inhalation
    - d. Chemical Burns
    - e. Noise
    - f.  $\text{H}_2\text{S}$  and  $\text{SO}_2$
    - g.  $\text{COS}$  and  $\text{CS}_2$
    - h. Electrical
    - i. Other
- E. Plant Upsets
- F. Sulphur Storage and Transportation





## I THE INDUSTRY

### A. HISTORY

Alberta's first gas plant (with sour gas removal facilities) was constructed in Turner Valley in 1933 for the conservation of solution gas. In 1951 the Jumping Pound plant went on line and became the first plant to produce elemental sulphur in the province. Since that time sour gas production has increased to the present volume where gas from plants of this type comprises more than one-half of Alberta's natural gas production.

Whether measured by provincial, national or world standards, our gas industry is big and sour gas processing is a significant portion of this industry. In 1970 Alberta produced more natural gas than any American State with the exception of Louisiana and Texas. Total 1971 Canadian production was 5,270 MMCFD of natural gas, of which Alberta produced 4,400 MMCFD or 83%. More than 55% of Alberta's gas production was from plants processing sour gas.

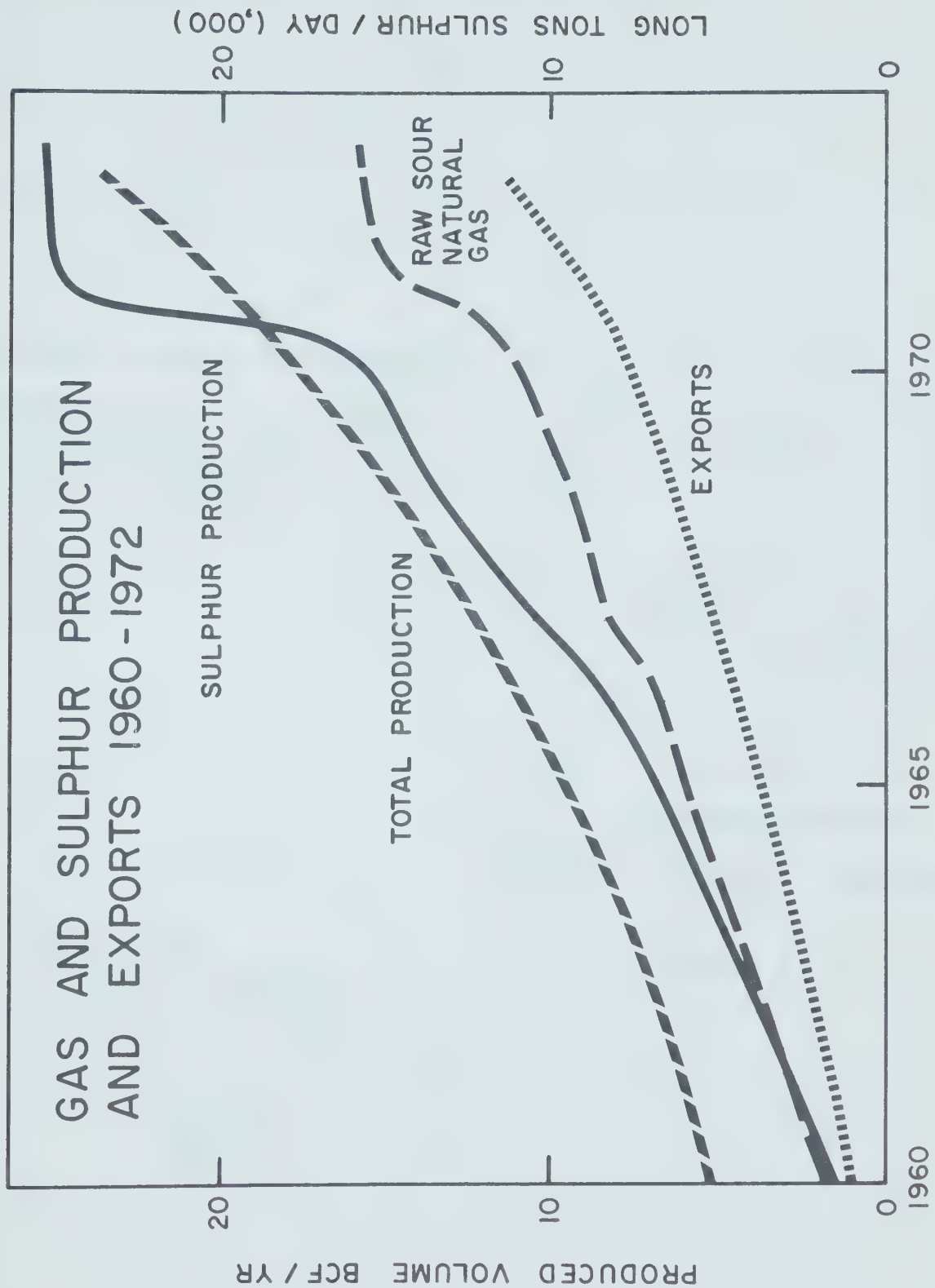
Figure I-1 through I-5 and Table I-1 show the growth and uses of Alberta and Canadian natural gas.

### B. FUTURE TRENDS

It is readily apparent that the reserves of petroleum, natural gas and sulphur in the province of Alberta are limited and finite. The ERCB has estimated that the marketable reserves of sulphur in sour natural gas will increase from the present 180 MMLT to about 240 MMLT in 1980, see Figure I-6. During this period sulphur production is expected to increase from 4.5 MMLT/year to about 10 MMLT/year.

Based on the current average sulphur recovery efficiency of 95%+, sulphur emissions in Alberta were 600 LTD. (.22 MMLT/



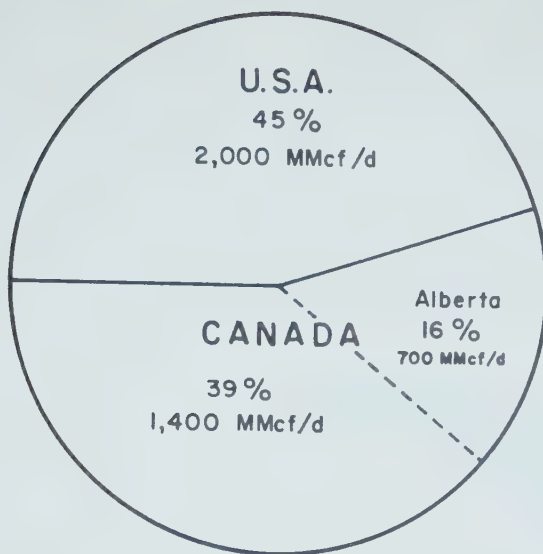


ADAPTED FROM "OILWEEK", Vol. 22, No.49, Jan.24, 1972, Page 41

Figure 1 - 1



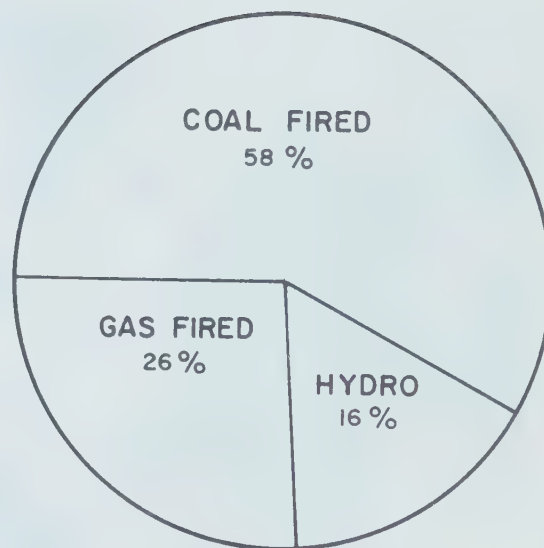




Total Gas Production 4400 MMcf/d

### DISPOSITION OF ALBERTA SALES GAS 1971

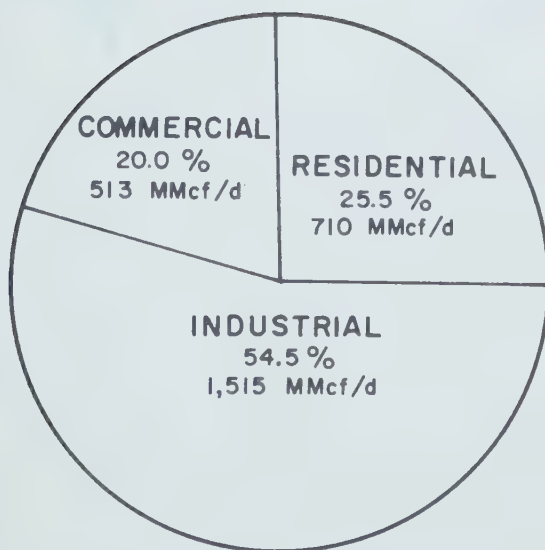
Figure 1 - 2



10,500 megawatt hours

### ALBERTA POWER GENERATION 1971

Figure 1 - 4



Total 2,800 MMcf/d

### TOTAL CANADIAN GAS CONSUMPTION 1971

Figure 1 - 3



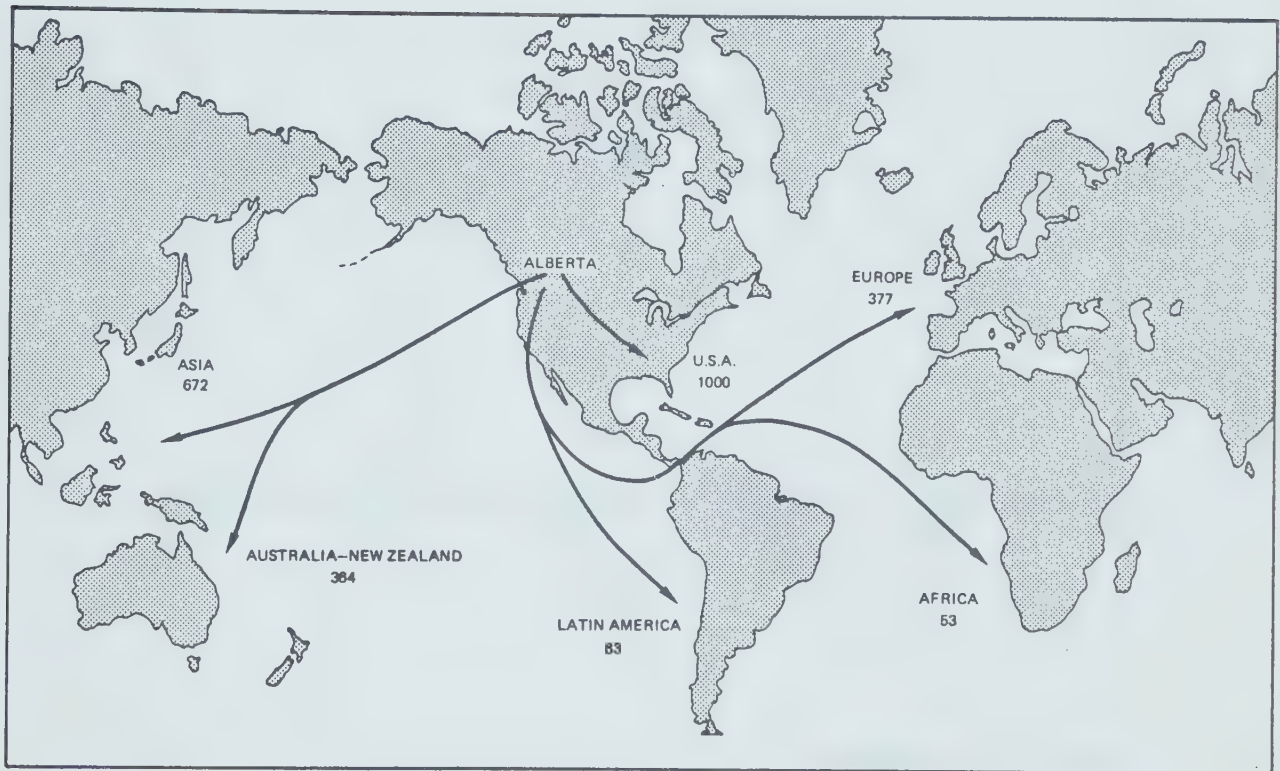


# 1970 ALBERTA SULPHUR EXPORTS - '000 LONG TONS

Sulphur shipments from Alberta to:

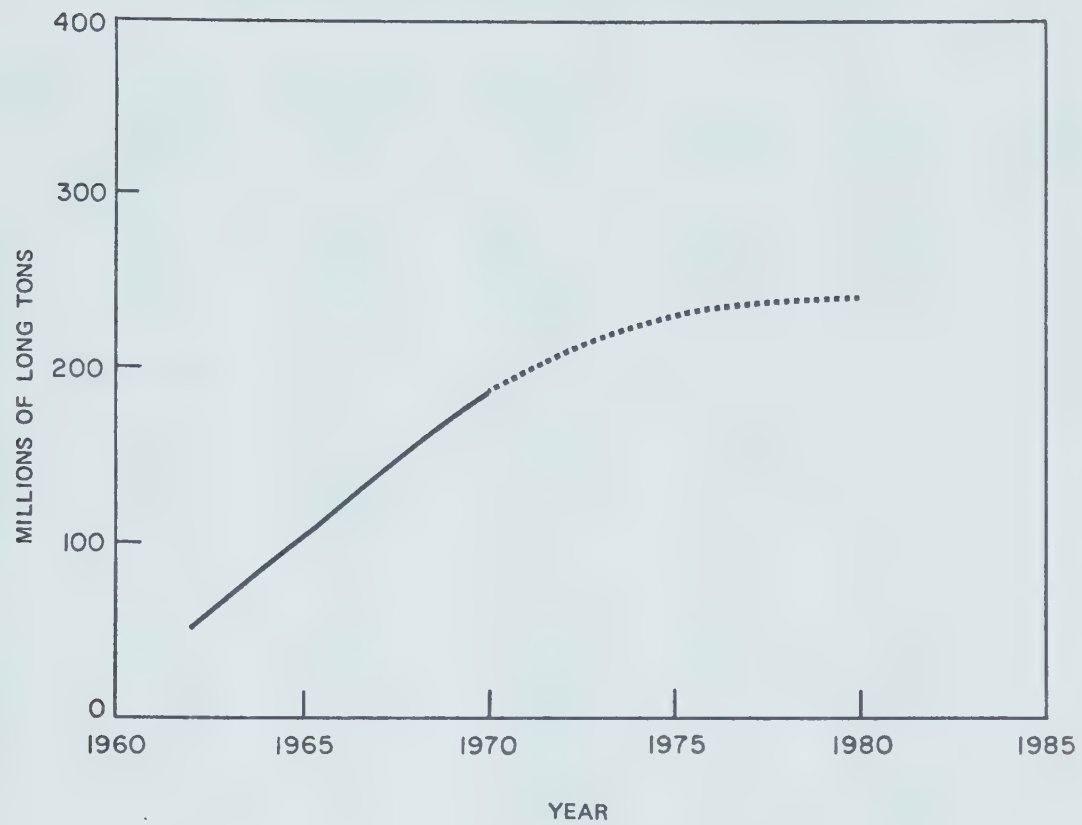
Other parts of Canada 375

Outside Canada 2530





## ALBERTA SULPHUR RESERVES



Source: Alberta Energy Resources  
Conservation Board.





GAS PLANT CAPACITIES (1956 - 1971)

<u>YEAR-END</u>	<u>RAW GAS GAS MMCF/D</u>	<u>RESIDUE GAS MMCF/D</u>	<u>PENTANES PLUS B/D</u>	<u>PROPANE B/D</u>	<u>BUTANE B/D</u>	<u>SULPHUR LONG TONS/DAY</u>
1971	13,670	11,560	260,100	118,400	72,500	24,750
1970	10,722	9,490	170,823	90,240	52,319	15,256
1969	10,050	8,911	161,747	80,510	47,169	14,330
1968	8,800	7,700	144,300	73,200	43,500	12,170
1967	8,360	7,360	127,500	58,300	39,300	10,600
1966	6,600	5,500	121,000	52,200	33,800	8,135
1965	6,100	5,200	112,000	42,000	30,600	7,100
1960	1,900	1,700	24,500	10,100	7,700	1,800
1956	450	300	5,700	4,300	3,200	127

( "OILWEEK" Jan. 24, 1972, Page 42 )



year) during 1971. This is equivalent to 3 lbs/acre when distributed over the province. Sulphur distribution at this rate is insufficient for arable areas to offset sulphur lost from the soil by removal of crops.

Projected sulphur emissions in Canada for 1970, 1975 and 1980 are detailed in Table I-2. Presently sulphur emissions from sour gas plants constitute about 6% of the total Canadian emission of sulphur. Table I-3 lists world-wide emissions of sulphur dioxide according to source while Figure I-7 illustrates comparative sources of  $\text{SO}_2$  in the U.S.A. The sour gas industry is included under the section marked "other". Figure I-8 shows the historical phases of sulphur production and Figure I-9 demonstrates recovered sulphur production from 1950 to 1971 in Canada, U.S.A. and France.

Exploration for new gas reserves in areas prone to sour gas (particularly in deep horizons and in the foothills area) is being inhibited by the poor rate of return that can be anticipated by any development follow-up. Development of reserves of sour gas may be restricted because of the considerable investment required to produce pipeline gas and low priced sulphur from such reserves.

Furthermore recent regulatory changes by the Energy Resources Conservation Board on plant sulphur recovery efficiency will increase sulphur plant costs very significantly and delay the day of development of additional gas reserves. Tables I-4 and I-5 briefly detail the economics of two existing field facilities and includes the probable investments required to meet ERCB sulphur recovery efficiency levels.

The Harmattan Leduc D-3 plant produces 7 MMCFD of sales gas and 480 LTD of sulphur from field gas containing 53%  $\text{H}_2\text{S}$ . Presently this plant is operating at a loss of approximately





\$90,000/year. Addition of tail gas cleanup to recover 98% of the sulphur will cost approximately \$1.2 MM and will increase the operating losses to \$210,000/year.

The East Crossfield Plant processes gas from the D-1 formation and produces 55 MMCFD of sales gas and 1570 LTD of sulphur. The plant has been in operation for more than four years and is still paying out the owner's original investment.



# **CANADIAN SULPUR EMISSIONS AND RECOVERY** (millions of long tons)

Source	1970		1975		1980	
	Total	%	Total	%	Total	%
	Recov'd.	Recov'd.	Recov'd.	Recov'd.	Recov'd.	Recov'd.
Metallurgical processes <sup>a</sup>	3.32	0.84	4.43	3.01	5.22	4.72
Coal Combustion <sup>a</sup>						
Electric Utilities	0.21	0	0.33	0	0.52	0
Other	0.26	0	0.20	0	0.19	0
Sub-total	0.47	0	0.53	0	0.71	0
Oil Processing & Combustion <sup>a</sup>						
Heavy fuel oil	0.44	0.10	0.59	0.35	0.82	0.59
Refining & other products	0.16	0	0.21	0.04	0.26	0.06
Sub-total	0.60	0.10	0.80	0.39	1.08	0.65
Sour gas processing	0.24 <sup>b</sup>	0	0.33	0	0.30	0
Tar sands processing	0.07 <sup>b</sup>	0	0.07	0	0.07	0
Other <sup>a</sup>	0.03	0	0.03	0	0.04	0
Grand Total	4.83	0.94	6.20	3.40	7.42	5.38
						73

Sources:

- a) Dept. of Industry, Trade & Commerce  
Ottawa.
- b) Alberta Energy Resources Conservation  
Board.





WORLD-WIDE ANNUAL EMISSIONS OF SULPHUR DIOXIDE  
(as calc'd. for 1965)

<u>Source</u>	<u>SO<sub>2</sub> Emission</u>	(Calc'd. as S)
	million long tons	% of total
Coal*	45.3	70.
Petroleum Combustion		
Gasoline	0.16	0.25
Kerosene	0.11	0.17
Distillate	0.90	1.4
Residual	9.05	13.9
Petroleum Refining	2.53	3.9
Smelting**		
Copper	5.8	8.9
Lead	0.67	1.0
Zinc	0.59	0.9
Total	65.1	100.

\*Includes lignite.

\*\*Excludes nickel smelting (figures not available).

Calc'd. from:  
E. Robinson & E.C. Robbins, (1)  
Stanford Research Institute



SO<sub>2</sub> EMISSIONS IN MILLIONS OF TONS (annually)

# COMPARATIVE SOURCES OF SO<sub>2</sub> - U.S.A.

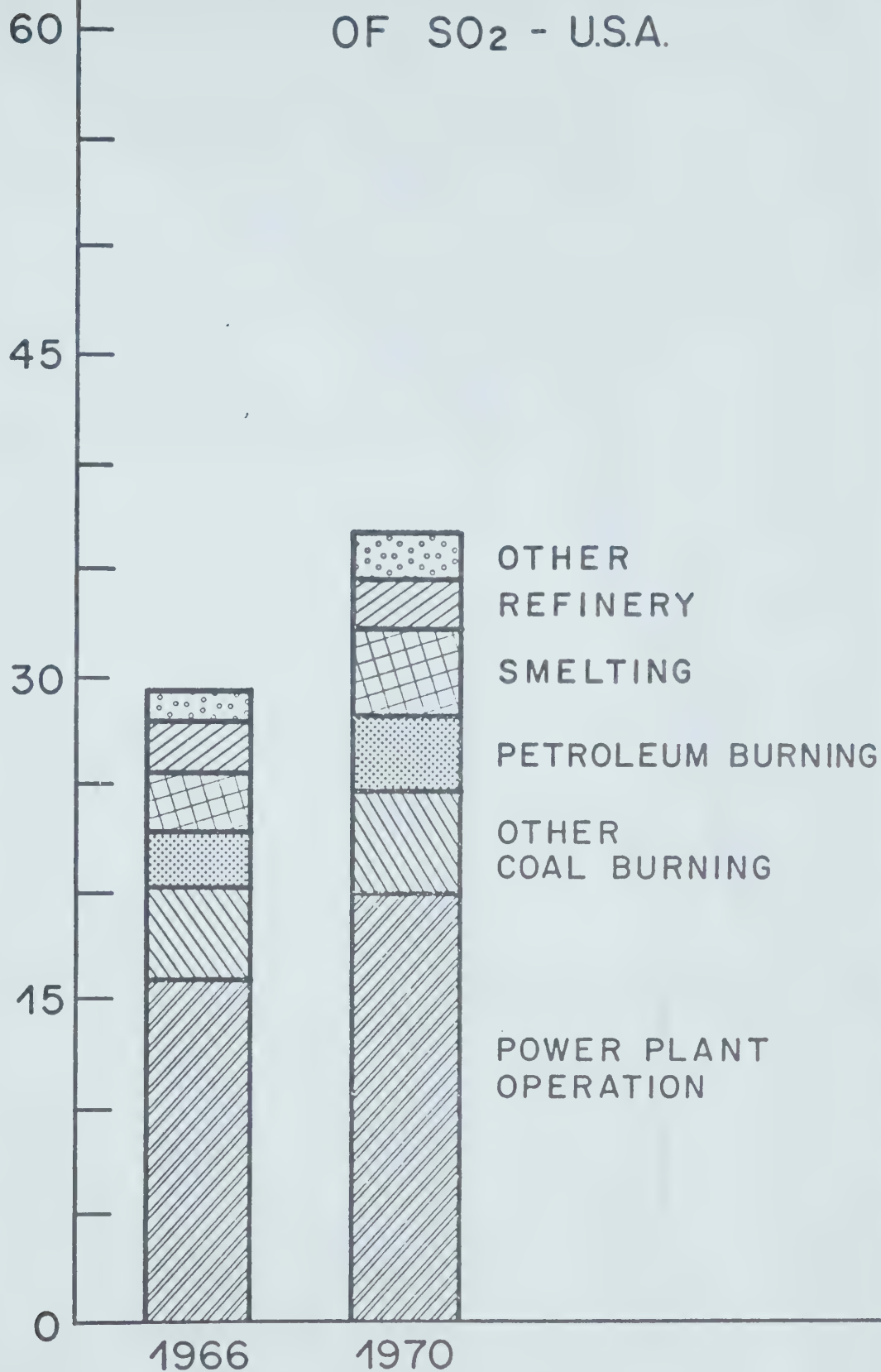


Figure 1 - 7





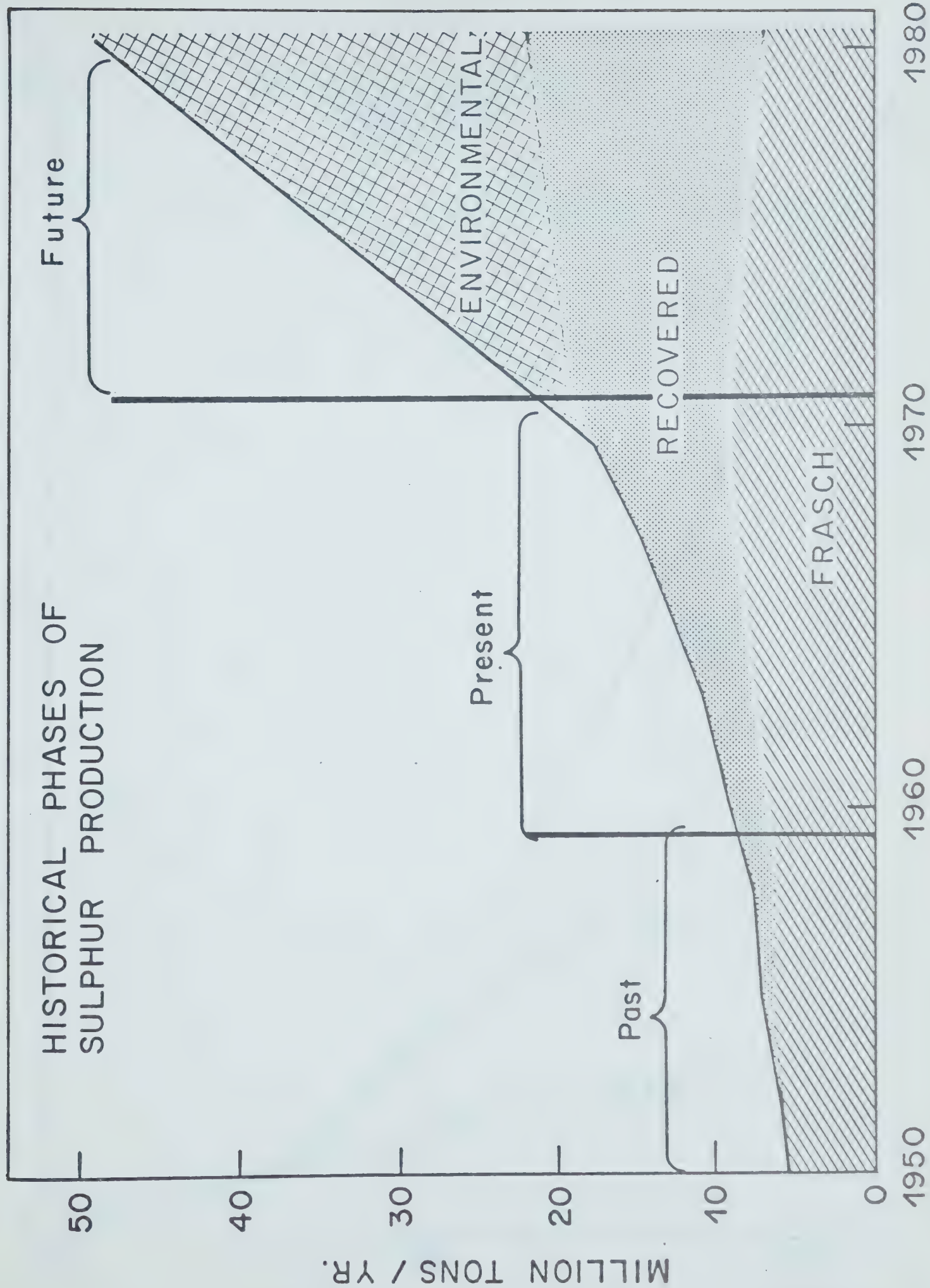


Figure 1 - 8



RECOVERED SULPHUR PRODUCTION  
(1950 - 1971)

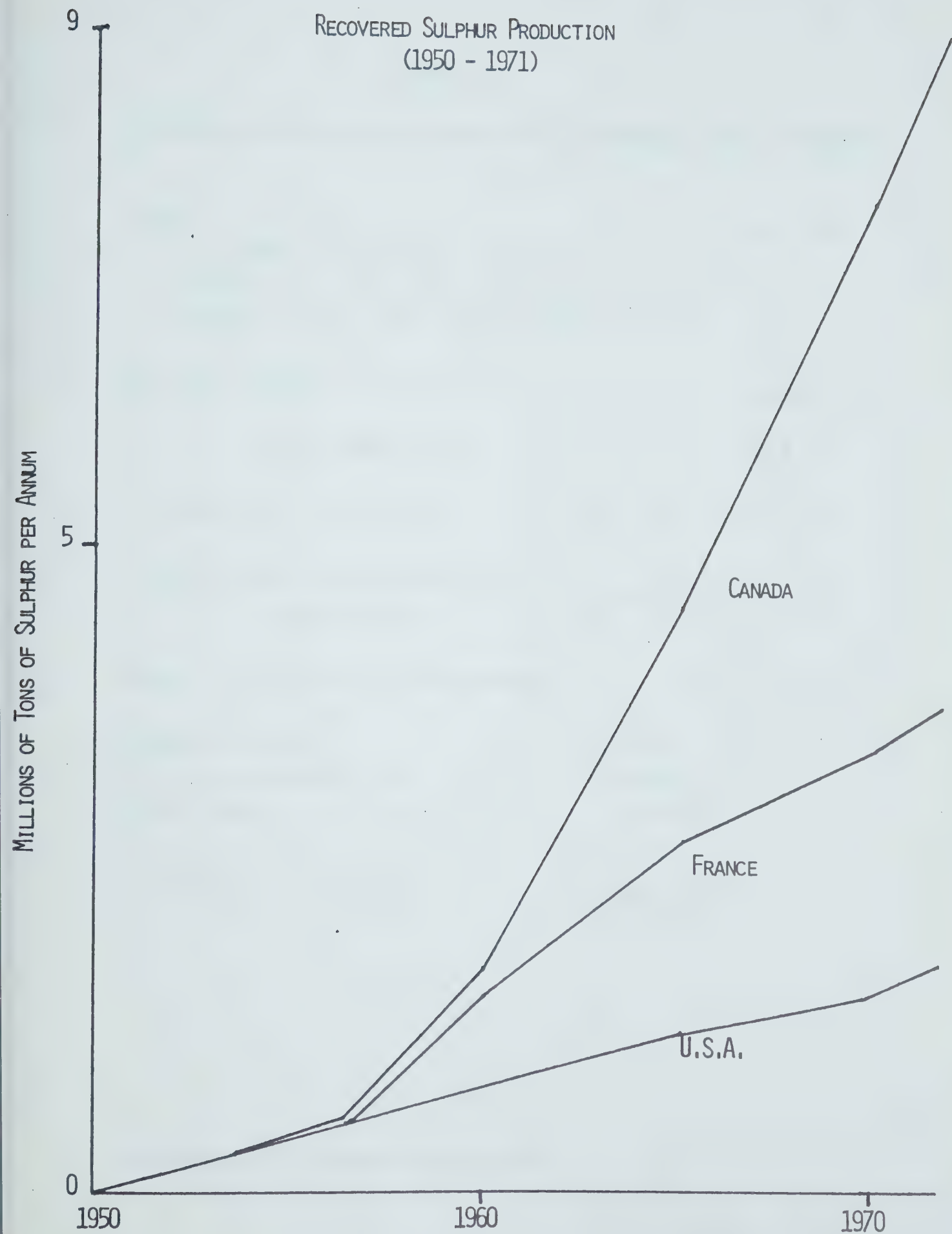


Figure I - 9





TABLE I-4

Harmattan Leduc D-3 Field and Gas Processing Plant Economics

Initial Investment	\$12.8 MM
--------------------	-----------

Includes development, drilling, lease  
aquisition costs, gas gathering systems,  
wellsites, gas plant and sulphur plant.)

Tail Gas Cleanup (projected)	<u>1.2 MM</u>
------------------------------	---------------

TOTAL INVESTMENT	\$14.0 MM
------------------	-----------

Revenues to December 1970	\$23	MM
---------------------------	------	----

Operating Costs to December 1970	7	MM
----------------------------------	---	----

NET REVENUES	16	MM
--------------	----	----

Return after payout of investments	2	MM
------------------------------------	---	----

Present Income	1.4	MM
----------------	-----	----

Present Operating Costs	1.5	MM
-------------------------	-----	----

Annual Loss	90,000
-------------	--------

Projected Tail Gas Plant
--------------------------

(Annual Operations)	120,000
---------------------	---------



TABLE I-5

East Crossfield D-1 Gas Processing Plant Economics

Development drilling	\$8.5 MM
Dry Hole Cost (Industry average)	1.0 MM
Lease Aquisition	2.5
Gas Gathering System & wellsite	5.0
Gas Processing Plant	14.0
Sulphur Plant	<u>8.0</u>
 Total Development	 \$ 39.0 MM
 Tail Gas Cleanup (projected)	 <u>3.5 MM</u>
 Projected Total	 \$ 42.5 MM
 Net Investment recovered by December 1971	 \$ 31.5 MM
 Annual Revenue (1971) before Tax and Royalties	 \$5.0 MM
 Annual Operating Costs (1971)	 2.3 MM
 Annual Operating Cost Tail End Plant (projected)	 0.8



## C. ECONOMICS

### 1. PLANT ECONOMICS

Production statistics for 1971 indicate that more than 55% of the gas processed in Alberta is obtained from sour gas fields. Sour gas and its attendant sulphur plants are an important segment of the Alberta and Canadian energy scene. Unfortunately, however, at the present gas and sulphur prices sour gas plants have become less and less attractive from an economics viewpoint.

Revenues to be received from condensate, LPG and natural gas can be estimated with a satisfactory degree of accuracy for the evaluation of a gas processing plant investment. Plants processing sour gas however, and receiving a considerable portion of their revenue from the sale of sulphur pose a prediction dilemma. The per cent of the total plant income from sulphur production increases as the gas increases in acid gas content and as the gas become dryer. At present sulphur prices, very sour natural gas decreases the quantity of residual gas and L.P.G.'s available for sale and at moderate to high concentrations is capable of reducing income to the point of making the projected operation an economic failure. Industry and indeed company estimates are at considerable variance concerning the future price of sulphur. The present price performances of sulphur Figure I-10 and the projected future growing oversupply (Figures I-11,12) are considerations which indicate no early increase in sulphur prices is to be expected.

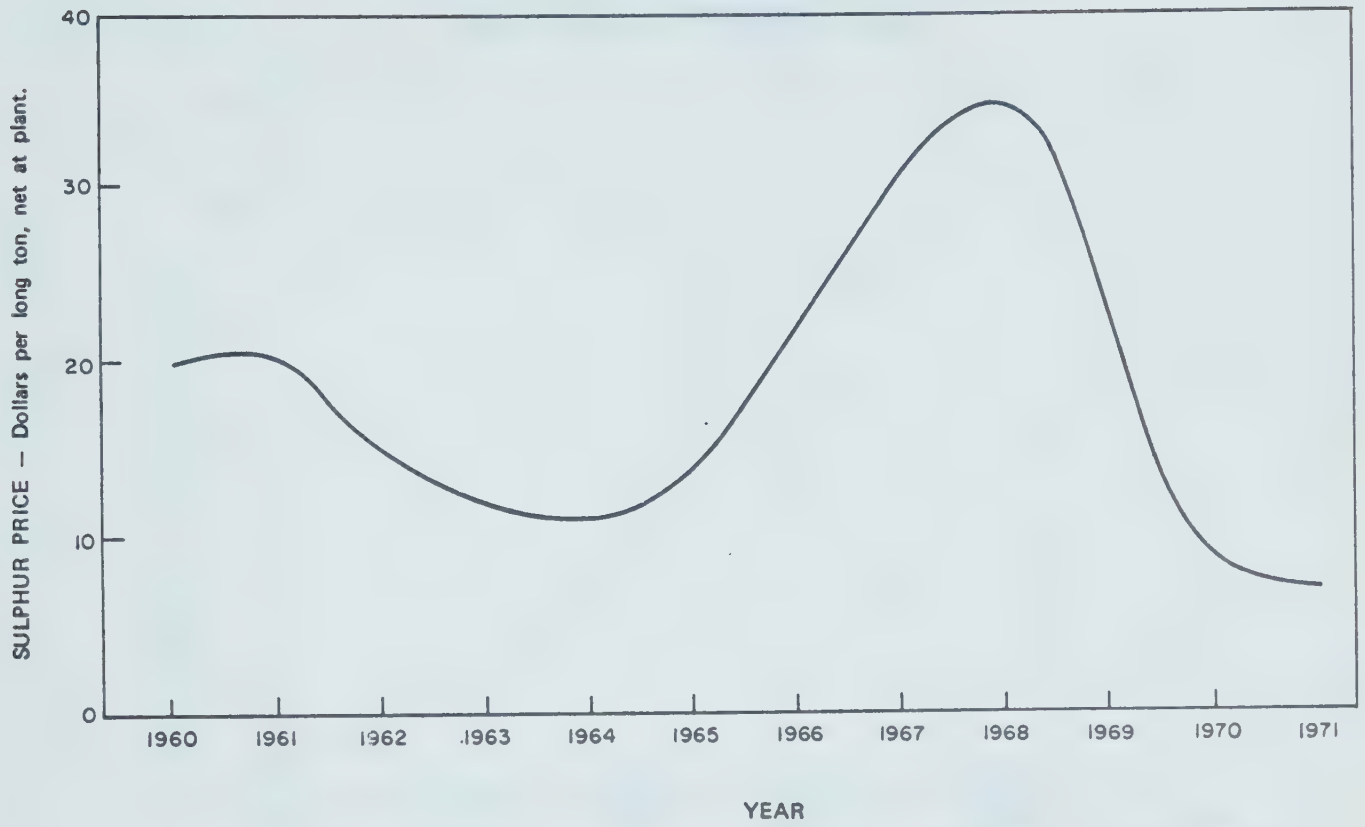
### 2. ECONOMIC BENEFITS TO ALBERTA

The benefits to Alberta from the natural gas industry are well documented. Expenditures in the province during 1971 are detailed below. For 1971 gross production revenues from natural gas were \$465 MM or 30% of the petroleum industry revenue of





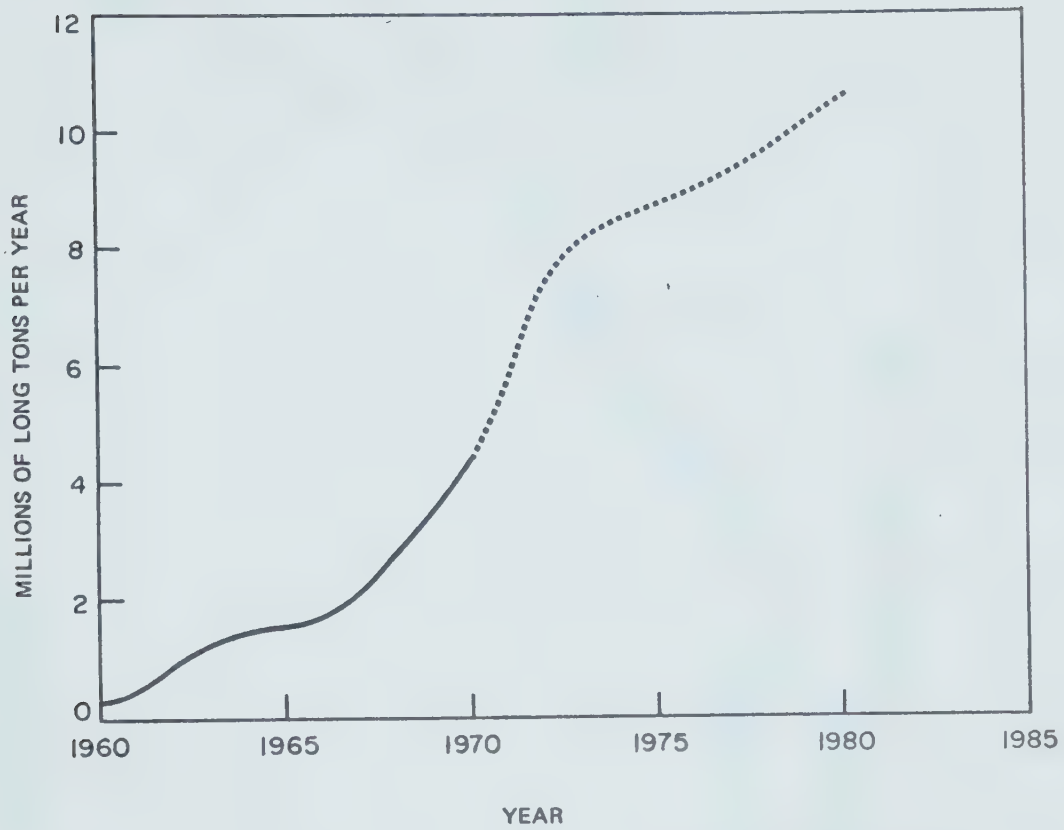
### NET PLANT PRICE OF ALBERTA SULPHUR



Source: Alberta Energy Resources  
Conservation Board.



## PRESENT & PROJECTED ALBERTA SULPHUR PRODUCTION



Source: Alberta Energy Resources  
Conservation Board.





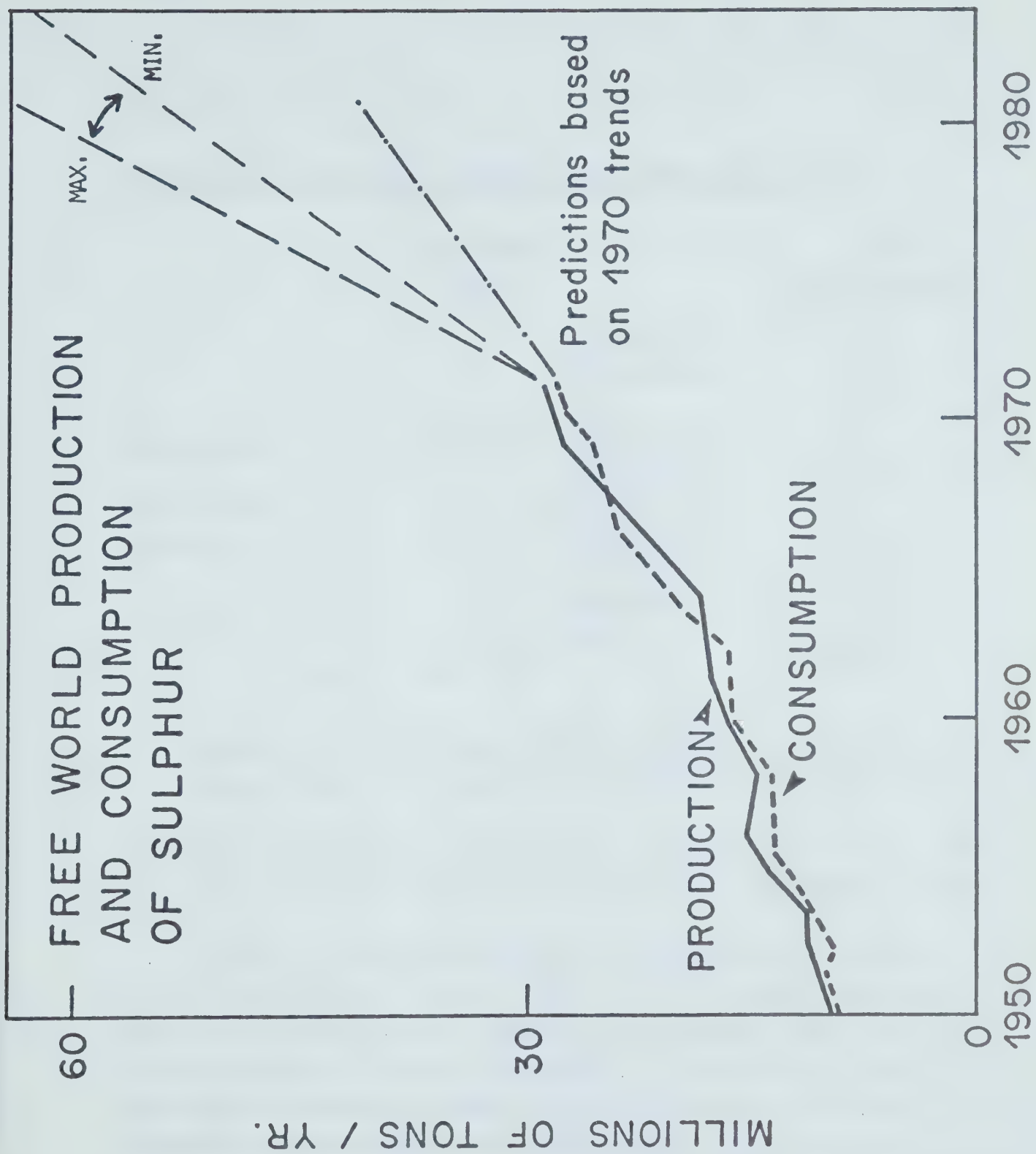


Figure 1-12



\$1555 MM.

NATURAL GAS INDUSTRY REVENUES AND EXPENDITURES 1971

	REVENUES		1971
	<u>1971</u>		<u>EXPENDITURES</u>
		EXPLORATION	\$26*
		DEVELOPMENT	12*
		LAND	18*
NATURAL GAS	\$263 MM	PRODUCTION FACILITIES	16*
GAS LIQUIDS	183	GAS PLANTS	207
SULPHUR	19	PRODUCTION COSTS	64**
		ROYALTIES	59**
		OTHER	30**
	<u>\$465 MM</u>		<u>\$432 MM</u>

\* Based on industry expenditures Oilweek February 21, 1972 prorated to natural gas on the basis of reserves discovered

\*\* Based on industry expenditures Oilweek February 21, 1972 prorated to natural gas on the basis of production value.

A major portion of industry expenditures are made in Alberta and create jobs not only in the industry but also through the "multiplier" effect for Canadians and Albertans. A study of E. J. Hanson, Professor of Economics at the University of Alberta in 1966 concluded that the petroleum industry directly and indirectly was responsible for generating 47% of the total personal income of Albertans in 1964. The increase over the years in the contributions by the petroleum industry to personal income is illustrated in the following Table:



PERCENT OF TOTAL PERSONAL INCOME IN ALBERTA

<u>INDUSTRY</u>	<u>1947</u>	<u>1952</u>	<u>1957</u>	<u>1964</u>
PETROLEUM	5	28	45	47
AGRICULTURE	75	56	37	35
OTHER	<u>20</u>	<u>16</u>	<u>18</u>	<u>17</u>
	100	100	100	100

Reference: E. J. Hanson, Regional Employment and Income  
Effects of the Petroleum Industry in Alberta.

We would estimate that currently 50% of personal income in Alberta has as its base the petroleum industry and that 30% of this figure is attributable to the gas producing and processing segment.

Presently oil and natural gas revenues constitute 21% of the gross provincial product while 30% of the revenue raised by the provincial government from within the province is supplied by the oil and gas industry.

D. INDUSTRY SAFE OPERATING PRACTISES

1. GENERAL

All drilling and production operations whether they pertain to hydrogen sulfide involvement or not, are subject to both government regulations and company standards and practices. Regulations governing drilling, production and pipelines are administered by the Energy Resources Conservation Board. Operations within forested areas are scrutinized by the Department of Lands and Forests. The Department of the Environment has jurisdiction over phases of drilling and production operations as they affect the environment. Regulations of these three government





bodies cover safety aspects and prudent operation of wells and pipelines to minimize environmental disturbances and maximize environmental protection. The gas industry has developed and uses many programs and standards in excess of the general government standards to provide for the safety of personnel, residents of the area, and for the protection of the environment.

## 2. DRILLING

During drilling, contamination of potable subsurface water is prevented by installing and cementing surface casing to a depth below the zone of interest or at least equivalent to 10% of the well's projected depth. Surface pollution from the drilling operation is prevented by maintaining proper drilling fluid systems, by the use of blowout preventers, and by adequately disposing of mud, cuttings and debris native to the operation.

Mud properties are carefully controlled to maintain an optimum drilling rate and still control formation pressures. If a blowout (formation fluid flowing into the well bore) occurs, the drilling rig is equipped with blowout preventers which can be closed to shut in the well. On completion of the well the drilling fluid is separated into liquid and solid portions. The liquid is approved for disposal based on the chemical composition following treatment. The dried solids are buried in the mud storage pit and the drilling site is restored subject to ERCB, Department of Lands and Forests and Department of Environment approval.

## 3. PRODUCTION OPERATIONS

In dealing with very sour wells employees work in pairs with emergency equipment available in their truck. Some operations have regular radio checks to keep the plant office in touch with field personnel.



Recent regulations by the ERCB require that safety shutdown valves be installed in the tubing of sour gas wells. These valves must be located at least 100 feet below the surface and automatically shut off the tubing in the event of uncontrolled rates of flow. In addition, sour gas wells are equipped as required with low and high pressure actuated shutdown valves on the well head to protect the transmission line from excessive pressures and to shut in the well in the event of a line failure.

#### 4. PIPELINE

The pipelines which transport the well bore fluids to the plant may be subject to failure caused by excessive pressure, corrosion, both interior and exterior, and mechanical interference.

Specifications for pipe for sour service are quite rigid. Experiments and experience have provided metallurgy and testing techniques which are used by the industry to provide safe and efficient sour gas transmission. These include pipe material specifications, hardness, manufacturing processes, welding techniques and inspection, such as X-ray and pressure testing.

Virtually all sour gas pipelines are externally coated and cathodically protected to minimize exterior corrosion. Interior corrosion is controlled by use of one of many types of corrosion inhibitors injected into the pipeline or periodically batched through it. As corrosion cannot be completely controlled, operators carry out extensive corrosion monitoring programs. Corrosion coupons and hydrogen probes are used to measure interior corrosion rates and evaluate inhibitor programs. Bell holes, ultrasonic and X-ray inspection are used to monitor interior and exterior corrosion. Test spools are also used.



TABLE I - 6

WORKMEN'S COMPENSATION BOARD ASSESSMENT RATES

1972 ( per \$100 of payroll)

1.	Underground coal mining	\$ 9.00
3.01	Logging, pulp and paper	\$ 8.00
3.02	Lumber mills	\$ 5.00
39.46	Farming	\$ 5.00
6.07	Highway construction	\$ 3.50
6.01	General oilfield construction	\$ 2.75
6.03	Painting, plastering	\$ 2.50
15.09	Oilfield service	\$ 2.25
6.02	Plumbing	\$ 1.80
89.01	Employment by towns, villages	\$ 1.70
	Employment by cities	\$ 0.95
2.01	Garage and service stations, auto repairs	\$ 1.20
39.08	Hotels, restaurants, drive-ins, catering	\$ 0.80
15.11	<u>Refineries, absorption plants</u>	
*	<u>includes gas plants</u>	\$ 0.60
11.02	Hardware, sporting goods stores	\$ 0.40
11.01	Department stores, drug stores	\$ 0.20
15.08	Operation of gas or oil wells	\$ 0.15





Regular leak detection surveys are also carried out.

## 5. PLANT OPERATIONS

### a. General

Gas processing plants are potentially dangerous work environments. The plants handle inflammable, poisonous fluids under high pressure, using high voltage electrical equipment, heavy equipment and rotating machinery, steam and chemicals. The gas industry and government have recognized these potential hazards and have set up stringent regulations and extensive safety programs that have succeeded in minimizing plant health hazards and accidents. The Workmen's Compensation Board assessment rates, Table I-6, are a reflection of the costs of accidents and are directly related to the severity and number of accidents in various industries. The sour gas processor have always emphasized safety and the low assessments for gas plants indicate that this policy has been successful.

Some gases are recognized as dangerous substances to be handled with respect. Every company working with very sour gas gives their personnel instruction and training on the detection of  $H_2S$ , rescue, safety and first aid procedures, as well as training to deal with any plant or field emergency involving this gas. Safety and rescue equipment must readily accessible, and periodically checked to insure that it functions properly. Safety drills are conducted to simulate emergency situations to familiarize personnel with corrective measures. Every plant processing sour gas is required to have an emergency procedure to deal with an uncontrolled flow of sour gas to protect personnel, area residents and process or field equipment.

Principle hazards in gas plants are failure of pressure equipment, fire, electrical shock, mechanical equipment failure,



H<sub>2</sub>S inhalations, chemical burns or inhalation and noise. Plant safety is concerned with prevention of accidents and minimizing the effects of accidents. Following are references to critical plant areas of concern.

(b) Explosions and Fire

A number of professional and governmental agencies have regulations and procedures for the standards of construction, among these are the Alberta Boilers Branch, American Society of Mechanical Engineers, American Petroleum Institute, American Society for Testing Materials, National Building Code, Canadian Electrical Code, Alberta Electrical Code, Canadian Standards Association, American Standards Association, American National Standards Institute, Canadian Insurance Underwriters, Workmen's Compensation Board and Department of Labor. These groups set standards for pipes, valves, fittings, vessel design and fabrication, installation, testing and maintenance. In addition, a regular program of corrosion control and monitoring as well as maintenance programs are carried out. Some plants have installed gas leak detectors and fire detection systems which in some cases are tied into plant safety and shutdown systems. The operators of gas plants have built up an extensive technology which is incorporated into the construction of the plant to increase safety and decrease the probability of equipment failures.

Individual companies and insurance underwriters have set standards regarding spacing and equipment and fire protection measures. Electrical conduits are sealed when entering hazardous areas to prevent explosions from traveling between areas. Plants are laid out to separate various pieces of equipment and processes to prevent fire damage in one area from spreading to another. Fire shutdown systems and 'panic buttons' are installed to decrease the fire size and spread. Fire extinguishers and fire water



systems are provided as required.

All employees are trained in fire drills for which the employee responsibilities and procedures are set out. Trained first aid personnel and equipment are available. At larger plants ambulances are available and the emergency procedures detail routes to hospitals, etc.

c. H<sub>2</sub>S Inhalation

Hydrogen sulphide is an ever-present hazard in sour gas plants. Safety meetings and equipment demonstrations are provided to keep the employees up to date. Work procedures are arranged so that men in hazardous area work in pairs or groups. When working on equipment that involves venting even small quantities of hydrogen sulphide, air masks are required. In buildings, warning lights are activated if maintenance is being done where H<sub>2</sub>S may be vented.

Buildings containing sour gas are supplied with forced ventilation to prevent accumulations of H<sub>2</sub>S. Maintenance procedures are set out to be followed to ensure safe working habits.

Plant designs incorporate open and closed drain systems. The closed door drain system prevents H<sub>2</sub>S vapours from accumulating in the plant area.

Prompt action is the key to saving a man who has been knocked unconscious by hydrogen sulphide. Every employee is instructed on rescue procedures and one or more resuscitators complete with oxygen bottles are always available.





d. Chemical Burns

Special instructions are given for the handling of dangerous chemicals and special handling equipment and protective clothing are provided if required. Some of the chemicals involved are sulphuric acid, sodium hydroxide, amines, lime, bacteriacides, fungicides and herbicides. Eyewash fountains and showers are provided, and First aid personnel are available to help in the event of a mishap.

e. Noise

There is considerable evidence that excessive noise can cause progressive hearing loss. Plant noise levels and employee exposures must be below the requirements of the Department of Labor. Noise surveys may be carried out as a matter of course and hearing protection is available, when required, for extended periods of work in noisy areas. More attention is being paid to the design of facilities and equipment to lower noise levels. Some companies have begun regular tests of employees exposed to high noise levels on a regular basis to ensure that hearing is not being impaired.

f. H<sub>2</sub>S and SO<sub>2</sub>

The American Conference of Government and Industrial Hygienists has set limits for these gases in work areas. Threshold limit values or values acceptable eight hours a day, five days a week, have been set at 10 PPM for hydrogen sulphide and 5 PPM for sulphur dioxide. No work area limits have been set by government in Alberta. Air contaminants in sour gas plants are not to be compared with urban smogs. The chemical composition of smogs, etc., is very complex



while a gas plant environment is much simpler. All evidence to date indicates that hydrogen sulphide and sulphur dioxide are not cumulative poisons and do not accumulate in the body. There is no evidence to indicate that the levels of hydrogen sulphide or sulphur dioxide usually encountered in gas plants can be connected with a progressive deterioration of health.

Hydrogen sulphide and sulphur dioxide in high concentrations cause eye irritation, lung irritation, headaches and can be fatal. Employees likely to be exposed to such high concentrations in specialty operations are required to wear air masks.

g. COS and CS<sub>2</sub>

COS and CS<sub>2</sub> are present in some sour gases and plant tail gas as trace components. These are not health hazards in the concentrations encountered. Any employee exposed to dangerous concentrations of these agents from the gas stream has already been exposed to a fatal concentration of hydrogen sulphide or sulphur dioxide.

CS<sub>2</sub> is used as a solvent to dissolve sulphur deposits in flow lines and downhole equipment. It is handled as a toxic chemical with toxic fumes. Department of Labor and company regulations cover the handling, use, and storage of this chemical.

h. Electrical

The Canadian and Alberta Electrical Code provide extensive regulations that ensure that safe systems are installed. Most gas plants have buried wiring to eliminate the hazards of overhead wiring. Basically no employees other than electricians are allowed to work with live electrical equipment. Special controls and



and systems are required in hazardous areas.

i. Other

Selenium and lead have never been detected in natural gas plant waste streams. Phenols, glycols, mercury and mercaptans may be found only in trace quantities and are not considered to be a health hazard.

All plant employees are encouraged to take first aid training and these courses are made available to employees through the St. John's Ambulance Society and Workmen's Compensation Board. First aid rooms and supplies are situated in the plants with competent men available to handle first aid situations. Programs of safety glasses, hats and steel-toed boots are in effect. All operators investigate all lost-time accidents to determine the causes and make recommendations to prevent such future accidents and injuries.

The record of gas processors with respect to in-plant safety speaks for itself. This position has not been achieved without considerable effort on the part of employees and industry organizations. Industry health and safety programs are an essential part of the operation of sour gas plants. These programs will continue in the future to deal with existing problems and to investigate and deal with any new areas of health concern that arise.

E. PLANT UPSETS

Interference in or disruption of the plant processing operation causing a "plant upset" condition is usually cited as an event responsible for abnormal emissions of sulphur compounds. Plant upsets generally are infrequent occurrences but also are a fact of life to be expected in the continuous operation of a multi-million dollar complex of valves, piping,





vessels, pumps, motors, furnaces, etc., handling varying loads of gas and liquid often in varying compositions under high pressures.

In sour gas plants, plant upsets usually cause sales gas to go off specification as regards  $H_2S$  content, and process streams must be diverted to the relief system and flare. Although instrumentation and alarms signal immediately the cause of the upset, permitting reduction or cessation of plant intake, even in the minor upset categories reconditioning of the plant system to "on spec" conditions can take considerable time. Often, in addition to time spent to correct the cause of the upset, lines must be depressured and absorbing chemicals reconditioned before a plant train can be returned to service.

Plant upsets are an inconvenience to the operator and in some instances a nuisance to plant area residents. In an endeavor to reduce the latter situation, high relief stacks with a perpetual flame are in service to emit and burn waste gases. Fuel gas is usually added to the waste gas to insure complete combustion of hydrogen sulphide to sulphur dioxide. These actions are the only practical methods available to date for handling these situations. In actuality, operators should be commended for their excellent record in maintaining plant operations under planned maintenance controls and schedules and reducing upsets in frequency and duration to the levels now experienced.

#### F. SULPHUR STORAGE AND TRANSPORTATION

Solid chemical sulphur is a remarkably friable material that is not totally chemically inert as far as interaction with the environment is concerned. For these reason problems of its storage and transportation can arise. Both have been tackled with some success by the industry as inventories have



increased and distant markets have been sought. Research continues to improve both storage and handling techniques.

Sulphur is generally stored in Alberta and elsewhere in solid form and until recently virtually all sulphur production in Alberta was cast into solid storage blocks at the plant site. These storage blocks were mechanically stable and dusting problems were primarily associated with loading and transportation. Chemical reaction with environment is primarily the result of interaction with water and air to yield oxidation products which are acidic in character. The range of contamination by these products of reaction of sulphur with environment is generally limited, however, and containment to the immediate vicinity of the plant operation has been generally good.

The sulphur dust problem associated with loading and transportation has been tackled by moving to "formed sulphur" and in particular slated sulphur. This technique was introduced generally in Alberta in 1971 and the bulk of Alberta production is now being slated. Research is continuing to attempt to improve the resistance to breakdown of formed sulphur and to examine the effects of aging which may well become significant if Alberta sulphur inventories continue to grow.

The bulk of Alberta sulphur shipments throughout North America are in liquid form. The industry recognised early the problems associated with the evolution of hydrogen sulphide from liquid sulphur during its storage and transportation. This problem has been successfully attacked and modifications continue to be made to minimise environmental contaminations from this source.

Work on the development of techniques for the pipeline transportation of sulphur is in progress. This is a potentially



important future development which may well bring Alberta's massive sulphur resources closer to world markets.





## II SULPHUR & SULPHUR COMPOUNDS - ENVIRONMENTAL EFFECTS

### A. Introduction

1. Scope
2. Sources of Sulphur Compounds in the Atmosphere
3. Role of SO<sub>2</sub> in life cycle

### B. Vegetation

1. Relative Susceptibility to Sulphur Dioxide
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  - (a) Sulphur Levels in Leaves - laboratory investigations.
  - (b) Field Observations.
  - (c) Vegetation Tolerance Limits
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### C. Animal Life

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1. Sulphur Dioxide
2. Oxidation Products of Sulphur Dioxide
3. Hydrogen Sulphide & Mercaptans

### E. Summary

1. Vegetation
2. Animal Life
3. Human Health

### F. References



## II SULPHUR & SULPHUR COMPOUNDS - ENVIRONMENTAL EFFECTS

### A. INTRODUCTION

#### (1) Scope

This section of the brief considers the effects of sulphur bearing compounds on: vegetation, animal and human health.

Primary consideration has been given to sulphur dioxide in view of the wide distribution of this compound in the atmosphere. Hydrogen sulphide will be briefly considered only, as it is normally oxidized to sulphur dioxide prior to discharge with combustion products from industrial process stacks. Mercaptans constitute a potential local odor problem but do affect vegetation. In addition, the effects of air and water transported sulphur dust, on soils and ground waters are reviewed.

The sources of sulphur compounds and their role in the natural cycle will be considered briefly.

#### (2) Sources of Sulphur Compounds in the Atmosphere

Sulphur compounds are introduced into the atmosphere from a variety of natural and man-made sources. These compounds consist of sulphur dioxide, hydrogen sulphide, and oxidation or reaction products such as sulphuric acid and sulphates. The global circulation of sulphur compounds follows an intricate pattern in relation to the sulphur content of soils, vegetation, water (in rivers, lakes and



oceans) and the atmosphere. Sulphur is released from the weathering of igneous and sedimentary rocks, from the bacterial decomposition of organic matter in soils, rivers, lakes and oceans and from combustion of fossil fuels and various industrial operations.

The yearly circulation of S has been documented by numerous investigators through mathematical global models (1, 2, 3). The total amount passing through the atmosphere is estimated at 365 million tons per year. The industrial emission at present makes up only 11 percent of the total.

The principal sources of industrial sulphur dioxide are the combustion products of sulphur-containing fossil fuels to provide electric power, steam and heat; the smelting of sulphide ores, refining of petroleum products, sour gas processing, coke processing, sulphuric acid manufacture, and many other operations that utilize raw materials containing sulphur. Estimates in Table II-1 indicate the approximate emissions of sulphur dioxide to the atmosphere in 1969 in Canada from the combustion of fossil fuels.

Natural sources of atmospheric sulphur dioxide, many times greater in quantity than the emissions from industrial operations, are derived from the death and decay of vegetation of land and plankton in the oceans, as well as from animal organisms. In this natural sulphur cycle, the sulphur may be released as hydrogen sulphide which is oxidized to  $\text{SO}_2$  in the atmosphere. Active volcanoes release large quantities of sulphur dioxide to the atmosphere, including emissions from fumeroles and vents that are often found in volcanic regions.





TABLE II-1

Estimates of sulphur Dioxide Emissions in Canada in  
1969 from Combustion of Fossil Fuels

(Data on Consumption of Fossil Fuels and Petroleum Products  
from Statistics Canada)

SOURCE OF COMBUSTION	SULPHUR DIOXIDE EMISSION SHORT TONS
COAL	895,000
LIGHT FUEL OIL, NOS. 2 AND 3	270,000
HEAVY FUEL OIL, NOS. 4, 5 AND 6	689,000
DIESEL FUEL	32,800
MOTOR GASOLINE	73,600
KEROSENE, STOVE AND TRACTOR FUEL	16,300
NATURAL GAS	<u>169</u>
TOTAL	<u>1,976,869</u>



### (3) Role of SO<sub>2</sub> in Life Cycle

Sulphur dioxide in low concentration is a natural and essential component of the atmosphere, like carbon dioxide. Life would be impossible without sulphur and it is, therefore, an essential element for the growth of vegetation. It is a vital constituent of proteins and is present in many biologically active compounds such as methionine, cystine, glutathione, thiamine and thiocetic acid. The sulphur in leaves consists mainly of two forms, an organic sulphur fraction and inorganic sulfates. Whether the sulphur is absorbed from the soil through the roots as soluble sulphate or through the leaves from the air as sulphur dioxide, the final disposition of the element is the same in the case of non-toxic concentrations. However, sulphate from the soil is more effective as a nutrient than is airborne sulphur dioxide because of the greater mobility of sulphate in the plant.

On the average, one sulphur atom is necessary for every 16 nitrogen atoms, or one part by weight of sulphur for every 7 parts by weight of nitrogen. In the global cycle of sulphur, by far the largest amount of sulphur dioxide and sulphate is supplied by the oxidation in the atmosphere of hydrogen sulphide, released by the decay of plant life and decomposition of organic matter. This sulphate is returned to the land and the sea by rain and other forms of absorption and deposition.

Although coastal areas receive substantial amounts of sulphate from rain contaminated with ocean spray, inland continental areas are entirely dependent on sulphur oxides in the atmosphere and supplements through use of fertilizers. An average forest requires 20 lbs. of sulphur per acre for



new growth. About 15 lbs. per acre is returned to the soil in fallen leaves and branches. The net requirement is, therefore, 5 lbs. per acre plus the amount lost in drainage. Farm crops require more sulphur and some, like cabbages, need as much as 40 lbs. per acre.

In Central Alberta, rain and snow analyses suggest, according to a report by Summers and Hitchon<sup>(4)</sup> of the Research Council of Alberta, that between 2 and 6 pounds of sulphur (as sulphate) per acre are being deposited annually. Present levels of sulphur oxides in the atmosphere of Central Alberta would seem to be contributing insufficient sulphur to eliminate the deficiency which exists in this area.

## B. VEGETATION

### (1) Relative Susceptibility to Sulphur Dioxide

Extensive studies of the effects of this gas on susceptible species of plants have been published by Katz, et al<sup>(5,6,7)</sup> and by Thomas and co-workers.<sup>(8,9,10)</sup> Different species of plants vary widely in their susceptibility to damage by sulphur dioxide. These differences appear to be due principally to variations in the rate of absorption of this gas by their leaves. Sensitive plants are those with succulent leaves of high physiological activity, such as alfalfa, cotton, barley, rye, spinach and rhubarb. Plants with fleshy leaves and needles are inclined to be more resistant, except when they are freshly or newly formed.

The susceptibility of green plants to sulphur dioxide





is dependent upon concentration, duration and absorption factors, as influenced by a variety of environmental conditions. Leaves of plants are more sensitive to gas during periods of active growth, optimal soil mixture, daylight hours, summer temperatures above 40°F and below 85°F, and in other environmental conditions that favour a high rate of photosynthesis, transpiration and absorption. Conversely, the resistance of plants to gas increases with age, in darkness, in the period of dormancy extending from autumn through the winter and early spring months, and during periods of drought and excessive temperatures in the growing season.

Conditions in the environment that cause the stomata of the leaves to remain open will enhance the absorption of gas and render a particular species more susceptible to injury. These include high relative humidity, high light intensity (especially in the morning hours), adequate moisture supply from the soil and moderate temperatures. The existence of a relationship between the diurnal trend of stomatal apertures and susceptibility in plants was demonstrated by Katz et al.<sup>(2)</sup> Most species of plants close their stomata at night and are, therefore, much more resistant than in daylight. The stomata also close under conditions of moisture stress (low relative humidity and inadequate soil moisture).

The following data (Table II-2) indicate the effect of decreasing relative humidity on alfalfa and other susceptible plants. If maximum sensitivity at 100% relative humidity is assigned a factor of 1.0, the resistance to SO<sub>2</sub> increases by a factor of ten in an environment of dry air.



TABLE II-2

Effect of Relative Humidity on  
Susceptibility to SO<sub>2</sub> (M. D. Thomas)

RELATIVE HUMIDITY PERCENT	RELATIVE RESISTANCE TO SO <sub>2</sub> INJURY
100	1.0
80	1.12
60	1.30
50	1.45
40	1.85
30	3.2
20	5.5
10	7.7
0	10.0



The relative susceptibility of many plants to  $\text{SO}_2$  is illustrated by the data in Table II-3, compiled by Thomas and Hendricks.<sup>(10)</sup> The factor of 1.0 has been allotted to the most sensitive plants, such as barley, alfalfa and rye. Higher factors in other species indicate increasing resistance. These factors have been adjusted to correspond to optimum environmental conditions that would promote maximum sensitivity to  $\text{SO}_2$ .

(2) Scientific Criteria for Effects of  $\text{SO}_2$  on Plants

(a) Sulphur Levels in Leaves - Laboratory Investigations

Plants exposed to atmospheric sulphur dioxide concentrations during the growing season will show an accumulation of sulphur in healthy leaves. Katz<sup>(5)</sup> has stated: "Unless the concentration and exposure to gas and other (environmental) factors are known accurately, there is no quantitative relation between the increase in sulphur levels of plant tissue and the degree of injury, because the sulphur content is subject to great variation in normal plants". Many later investigators have confirmed Katz's conclusions, that foliar sulphur levels are not related to damage by sulphur dioxide. Some of these are Berry, G. R. et al<sup>(11)</sup>, Viel, M. G. et al<sup>(12)</sup>, Garber, K.<sup>(13)</sup>, Wentzel, K. F.<sup>(14)</sup>, and Bjorkman, E.<sup>(15)</sup>. Guderian<sup>(16)</sup> found that sulphur levels continue to fluctuate in the green photosynthesizing tissue of partially killed needles, whereas sulphur levels remained steady in the killed portions of such needles. Guderian further reported that foliar sulphur levels decrease after cessation of fumigations and are, therefore, not only dependent on rates of sulphur assimilation during fumigations but also on frequency and duration of sulphur dioxide free periods





TABLE II-3

Relative Sensitivity of Cultivated  
and Native Plants to SO<sub>2</sub> Injury

SENSITIVE		INTERMEDIATE		RESISTANT	
-cultivated plants-					
Alfalfa	1.0	Cauliflower	1.6	Gladiolus	2.6
Barley		Parsley		Horse-radish	
Endive		Sugar Beet		Sweet Cherry	
Cotton		Sweet William		Rose	2.8 - 4.3
Rye					
Cosmos	1.1	Aster		Potato	3.0
Rhubarb		Tomato	1.3 - 1.7	Castor Bean	3.2
Sweet Pea		Eggplant		Maple	3.3
Radish	1.2	Parsnip		Boxelder	
Verbena		Apple	1.8	Wisteria	
Sweet Potato		Cabbage	2.0	Mock Orange	3.5
Spinach		Hollyhock	2.1	Onion	3.8
Buckwheat	1.2 - 1.3				
Bean	1.1 - 1.5	Peas		Lilac	
Broccoli	1.3	Gooseberry		Corn	4.0
Brussels Sprouts		Marigold		Cucumber	4.2
Pumpkin		Leek	2.2	Crysanthemum	5.3 - 7.3
Table Beet		Begonia		Celery	6.4
Oats		Grape	2.3	Citrus	6.5 - 6.9
Clover	1.4	Linden		Cantaloupe	7.7
Rye Grass	1.4				
Squash		Peach		Live Oak	14.0
Carrot	1.5	Apricot		Privet	15.0
Turnip		Elm	2.4		
Wheat		Birch			
		Plum	2.5		
		Poplar	2.5		



between fumigations. Hence the timing of sampling for sulphur level determinations after exposure to sulphur dioxide becomes an additional variable factor. There is another complicating factor. Long periods of uninterrupted exposure to very low levels of sulphur dioxide cause greater increases in foliar sulphur levels than shorter periods of exposure to higher but still sublethal levels of sulphur dioxide (Guderian 16).

It is clear that foliar sulphur contents cannot be used as a measure of damage by sulphur dioxide. However, given a steady source of sulphur dioxide emissions, foliar sulphur levels may be indicative of the extent of sulphur dioxide dispersion. Katz <sup>(6)</sup> has noted: "Nevertheless, such data (foliar sulphur contents) from comprehensive collections of certain sensitive plants, may be used to define the area within which the gas occurs". Today, this is indeed the only "practical" use that can be made of knowledge of foliar sulphur contents obtained from field samples.

Loman <sup>(17)</sup> has reported that results of a cooperative study of the Alberta Forest Service and the Provincial Air Pollution Control Division showed that pine and spruce foliar sulphur contents fluctuated upwards in the vicinity of sour gas plants for 3 to 5 years, after which they fluctuated down again to levels found at the time the gas plants went into production, whereas foliar sulphur contents of aspen and poplar continued to fluctuate upwards (Ullman 18). From a biological point of view, the fluctuations in foliar sulphur levels in pine and spruce after 3 to 5 years exposure to sulphur dioxide may be ascribed to any of a considerable number of uncontrollable factors of the environ-



ment about which we have no information. From a practical point of view, sulphur dioxide emissions near the sour gas plants investigated by these agencies have up to now obviously been below the lethal level for the main tree species.

(b) Field Observations

The following data, (Table II-4) compiled by Dreisinger (19) and McGovern, indicate the minimal intensity factors prevailing at the time that recorded ground concentrations and durations caused injury to various species of agricultural and forest growth. The plant species are listed in order of increasing resistance to  $\text{SO}_2$ . It is apparent that buckwheat and trembling aspen are the most sensitive species in the Sudbury District, with a minimal intensity value of 74. These data represent correlations between field observations on the condition of crops, shrubs and trees and gas concentrations recorded at the nearest  $\text{SO}_2$  monitoring stations.

Intensity numbers were assigned to the above exposure limits on the basis of 100 being equal to the approximate threshold limit for injury under optimum sensitivity conditions for the most susceptible species of vegetation. Thus an average concentration of 0.95 ppm for one hour, or 0.55 ppm for two hours, or 0.35 ppm for four hours, or 0.25 ppm for eight hours would in each case be equal to a potential intensity of 100. Intensities above or below these limits of concentration and duration of exposure could then be computed by this formula.

A total of 5,602 fumigations recorded in the Sudbury area were analyzed on the above basis. Of these, 622 reached or exceeded the above threshold levels potentially capable of causing injury to vegetation. However, many of the 622 recorded fumigations did not cause any injury to susceptible species as they occurred either too early or late in the





TABLE II-4

Minimal average SO<sub>2</sub> concentrations recorded after which injury to vegetation was observed in various species and maximum intensities to which the species were exposed at other times with no resultant injury (Dreisinger and McGovern)

Species	Max. av. conc. (ppm for				Intensity Number	Max. intensity to which species exposed with no resultant injury
	1 hr.	2 hr.	4 hr.	8 hr.		
buckwheat	0.56	0.39	0.26	0.15	74	-
red clover	0.60	0.50	0.33	0.17	94	332
oats	0.63	0.59	0.34	0.17	107	294
peas	0.63	0.59	0.34	0.17	107	276
rhubarb	0.63	0.59	0.34	0.17	107	276
timothy	0.66	0.54	0.40	0.21	114	240
swiss chard	0.88	0.64	0.42	0.27	120	268
beans	0.46	0.45	0.43	0.21	123	272
beets	1.31	0.77	0.45	0.23	140	272
turnips	1.31	0.77	0.45	0.23	140	272
carrots	1.08	0.79	0.50	0.25	144	276
cucumbers	1.08	0.79	0.50	0.25	144	276
lettuce	0.64	0.56	0.43	0.38	152	276
radish	0.64	0.56	0.43	0.38	152	276
squash	0.64	0.56	0.43	0.38	152	157
tomatoes	0.64	0.56	0.43	0.38	152	272
potatoes	0.64	0.56	0.43	0.38	152	332
raspberry	0.74	0.63	0.53	0.39	156	332
celery	0.87	0.74	0.55	0.29	157	240
spinach	1.34	0.91	0.50	0.34	166	276
cabbage	0.94	0.89	0.70	0.45	200	332
corn	never injured <sup>a</sup>					294

<sup>a</sup> near recorder stations



TABLE II-4 (Continued...)

Minimal average SO<sub>2</sub> concentrations recorded after which injury to vegetation was observed in various species and maximum intensities to which the species were exposed at other times with no resultant injury (Dreisinger and McGovern)

Species	Max. av. conc. (ppm for				Intensity Number	Max. intensity to which species exposed with no resultant injury
	1	2	4	8		
- Forest Species -						
trembling aspen	0.42	0.39	0.26	0.13	74	450
jack pine	0.52	0.44	0.29	0.20	83	143
bracken fern	0.45	0.34	0.25	0.21	84	209
white birch	0.46	0.38	0.28	0.21	84	450
white pine	0.45	0.35	0.25	0.21	84	224
larch	0.41	0.38	0.34	0.26	104	160
large-toothed aspen	0.66	0.43	0.37	0.20	106	450
willow	0.41	0.38	0.33	0.30	120	332
alder	0.46	0.43	0.43	0.21	123	332
red pine	0.78	0.69	0.44	0.30	126	432
Austrian pine	0.66	0.45	0.44	0.33	132	432
hazel	1.14	0.75	0.45	0.23	136	192
balm of Gilead	0.95	0.68	0.61	0.38	175	332
cedar	never injured <sup>a</sup>				-	224
spruce	never injured <sup>a</sup>				-	450
maple	never injured <sup>a</sup>				-	450

<sup>a</sup> near recorder stations

Intensity numbers	(1)	105 x for 1 hr. where X represents SO <sub>2</sub> in ppm
	(2)	182 x for 2 hrs. " " " " " "
	(3)	286 x for 4 hrs. " " " " " "
	(4)	400 x for 8 hrs. " " " " " "



growing season, or during periods when the vegetation was comparatively resistant to  $\text{SO}_2$ . Only on nine occasions was injury observed after exposure to  $\text{SO}_2$  during which the average concentrations were lower than the listed potential limits. In every instance, such injury occurred with fumigations during the critical months of June and July in periods of high humidity and environmental factors favouring maximum susceptibility.

(c) Vegetation Tolerance Limits

Detailed studies on the effects of sulphur dioxide on photosynthesis, respiration, rate of growth and yield of the most sensitive plants, such as alfalfa, by Katz et al, and by Thomas and co-workers have lead to the following findings:

- (1) About 0.30 ppm applied to the plants for four hours per day for a month had no effect.
- (2) A whole crop of alfalfa was grown under continuous fumigation with an average concentration of 0.10 ppm for 504 hrs. and in another experiment, with continuous fumigation at 0.11 ppm for 602 hrs., without producing any injury and with no effect on photosynthesis, rate of growth and yield.
- (3) A 45-day continuous fumigation of alfalfa at an average concentration of 0.10 ppm showed no effect on carbon dioxide assimilation or growth.
- (4) At higher concentrations, 0.40 to 0.60 ppm for 4 hours, it was found that alfalfa showed a small reduction in carbon dioxide assimilation but





complete recovery occurred within about two or three hours after the fumigation was discontinued.

- (5) Under optimum environmental conditions for susceptibility, the first light symptoms of injury may occur in a fumigation of alfalfa with about 1.25 ppm in one hour.

On the basis of an extensive review of scientific evidence on the effects of sulphur dioxide on sensitive species of plants, the State of California adopted the following ambient air quality standards at the "adverse level" (15):

1.0 ppm for one hour, in daylight  
0.30 ppm for eight hours, in daylight

## (2) Effects of H<sub>2</sub>S

Hydrogen sulphide is usually not toxic to plants except in high concentrations greater than about 10 to 20 ppm. This gas has an offensive odour in concentrations as low as 0.05 ppm and may be detected by smell in the vicinity of oil refineries and draft pulp mills. Although it tarnishes metals and discolors paint at low concentrations, there is little, if any, evidence that this gas causes significant injury to field crops.

## C. ANIMAL LIFE

Early interest in this subject was concerned mainly with diseases and mortality in farm animals arising from the emissions of toxic metals from metal smelting and refining operations and the phosphate fertilizer industry. In the early



history of base metal smelting, cases of litigation developed over poisoning of livestock by arsenic, lead and some other heavy metals. However, the development of adequate methods of source control have virtually eliminated this hazard to animals. There are no substantiated cases on record of injury to farm animals from emissions of sulphur oxides in the metal smelting and refining industry in the last forty years. It is only within recent years that laboratory studies have been undertaken on a systematic basis to determine the toxic effects of animals of specific air pollutants commonly found in the community atmosphere. This interest has developed out of concern for the effects of air pollution on human health. Pollutants presently under investigation include sulphur dioxide, sulphuric acid nitrogen oxides, ozone and oxidants, carbon monoxide, aldehydes, organic peroxides and various potentially carcinogenic compounds.

With regard to the harmful effects of air pollution on animal health, the evidence of major air pollution disasters in urban areas points to adverse symptoms in animals of a character similar to those suffered by man.

There are only a few reports on long-term experimental exposure of animals to sulphur oxides in which pulmonary function measurements and related physiological parameters were measured. Dogs were treated by Lewis et al <sup>(20)</sup> for 225 days with 5.1 ppm SO<sub>2</sub>, 5.1 ppm SO<sub>2</sub> plus 835 micrograms/m<sup>3</sup> of sulphuric acid aerosol. The results of this study with far higher concentration dosages than those encountered in urban or industrial areas revealed that the exposed dogs had no significantly different values from control dogs for diffusion capacity, compliance, flow resistance or residual volume in lung function performance.



Another long-term study, reported by Vaughan et al<sup>(21)</sup>, involved dogs exposed for 16 hours a day for a period of 18 months to a combination of 0.5 ppm SO<sub>2</sub> and 100 ug/m<sup>3</sup> of sulphuric acid aerosol. No impairment of pulmonary function was produced in any of the animals after 18 months of exposure. In a third long-term study reported recently by Alarie et al.<sup>(22)</sup> three groups of guinea pigs were exposed to 0.13, 1.01 and 5.72 ppm of sulphur dioxide continuously for 12 months. Pulmonary function measurements with a high degree of precision indicated that no detrimental changes could be found from this prolonged exposure to SO<sub>2</sub> in any of the groups of animals.

It is apparent that with regard to natural gas processing and sulphur recovery operations in Alberta and in other industrial processes involving the emission of sulphur oxides under the present government control regulations, no health hazard exists from the relatively low ground concentrations that may be found in the vicinity of such operations.

#### D. HUMAN HEALTH

##### (1) Sulphur Dioxide

Studies of the health effects of urban air pollution have been stimulated by the consequences of a series of acute air pollution episodes that have been accompanied by increased mortality and morbidity among the exposed populations. These episodes occurred in the Meuse Valley of Belgium in 1930, Donora, Pa., in 1948, London (England) in 1952, 1956, 1957 and 1962, New York in 1953, 1963 and 1966, and in a number of large cities in Europe and Japan at other times.





Attempts to identify the agents responsible for the excess deaths and sickness in these acute episodes have not been successful. Most attention has been devoted to sulphur dioxide and particulate matter because these were the only contaminants for which concentration measurements were available at the time.

Human volunteers have been exposed for durations up to one hour by inhalation of diluted sulphur dioxide from 1 to 20 ppm and higher concentrations. Exposure to 4 to 5 ppm and higher does induce an increase in airway resistance in a majority of exposed individuals, according to studies by Frank (23, 24).

Medical personnel expose asthmatics and chronic bronchitic patients to high sulphur dioxide concentrations to determine their irritability to the inhalation. The concentrations used in these provocative tests range from 1200 to 4800 ppm in order to obtain a broncho-spasm response after a few breaths. These patients appear to tolerate these treatments without major consequences.

The theory that sulphur dioxide may condense on particles of respirable size to produce a high local concentration of gas at the site of impaction in the lungs has been proposed by Goetz (25). In tests of this hypothesis, small animals have been exposed to high concentrations of  $\text{SO}_2$  and activated carbon dust. The gas concentrations ranged from 116 to 212 ppm. No increase in ciliary inhibition was found, other than what could be expected from the inhalation of  $\text{SO}_2$  by itself. This absence of additive effect or of synergism appears to contradict the Goetz hypothesis.



The available data from epidemiological studies indicate that populations exposed to sulphur dioxide at significant levels of 0.5 to over 2 ppm, do not show direct evidence of increased susceptibility to respiratory infection deriving from the effects of  $\text{SO}_2$ . Major obstacles to the interpretation of epidemiological information health effects are the frequent lack of standardization of the populations that are being compared in terms of smoking, occupation and social history.

Burrows et al. (26) in a study of the relationship of symptoms of chronic bronchitis and emphysema to weather and air pollution concluded that sulphur dioxide is not specifically related to aggravation of chronic bronchitis and that air contaminants do not appear to play major roles in producing these aggravated symptoms. In a detailed study of hospitalization for diseases such as allergic disorders, acute respiratory infection, influenza and bronchitis in relation to air pollution, Sterling et al, (27) found a correlation factor of only 0.16 with sulphur dioxide, which is insignificant.

The amount of sulphur dioxide a human being can inhale and retain in serious episodes is not very great. A simple calculation will show that a man breathing sulphur dioxide steadily at 1 ppm will absorb, at most, 14 ml. of gaseous  $\text{SO}_2$  per 24 hours. This corresponds to a weight of about 37 mg. of  $\text{SO}_2$ , which in turn represents approximately 0.57 millimole per total body weight, of either sulphur dioxide or sulphurous acid. The latter is a well known weak acid resembling kinetically carbonic acid. The net result for the organism will amount to something less than one milliequivalent of acid, an aliquot which the organism can easily



dispose of. Normal kidneys, in fact, often eliminate well in excess of 20 milliequivalents per litre of urine as titratable acid. Thus, exposure to  $\text{SO}_2$  may result in lowering urinary pH. Acid urine, in fact, has been noticed in persons exposed to high levels of sulphur dioxide in industry <sup>(28)</sup>. However, these same levels, encountered in the past, in industrial exposures, are not at all comparable to those of air pollution occurrence in the outdoor atmosphere.

## (2) Oxidation products of sulphur dioxide

The industrial hygiene TLV of maximum allowable concentration for sulphuric acid mist (or sulphur trioxide) has been established at 1 milligram per cubic metre of air ( $1 \text{ mg/m}^3$ ) for workers exposed 8 hours per day, 5 days per week. Sulphur trioxide or sulphuric acid appears to be more of an irritant than sulphur dioxide at equal doses in man and in animals. Inhaling  $\text{H}_2\text{SO}_4$  with particle size of 0.8 micron, guinea pigs react with an increase of airway resistance when the concentration is equal or higher than  $1.9 \text{ mg/m}^3$ . Human volunteers exposed to sulphuric acid at concentrations in excess of  $2.9 \text{ mg/m}^3$  for one hour have complained of irritation of the conjunctivae and of the respiratory mucosae. Several subjects have shown increased airway resistance, measured by the interrupter technique <sup>(29)</sup>. However, exposing volunteers to  $1 \text{ mg/m}^3$ , Lawther has found no significant change in airway resistance <sup>(30)</sup>. Conversely, Toyama and NaKamura, using a similar concentration of sulphuric acid, have indicated a substantial change of resistive values in exposed subjects <sup>(31)</sup>.

The oxidation of sulphur dioxide to sulphur trioxide





or sulphuric acid in the ambient atmosphere is a slow process, with complex equilibrium constants, as shown by Katz (32, 33). Humidity, sunlight and the presence of nitrogen dioxide as well as catalysts in the atmosphere, all have an important influence on the rate of oxidation. However, the percentages of conversion of  $\text{SO}_2$  to sulphuric acid in the ambient atmosphere are usually in the range of 3 to 5 percent by weight, although under exceptional conditions the conversion may reach 15 to 35 percent. Measurements of sulphuric acid aerosol in polluted urban areas seldom attain levels above 0.05 to 0.10  $\text{mg/m}^3$ . In the London smog episode of December, 1952, the concentration of sulphuric acid was estimated to reach levels not in excess of 0.35  $\text{mg/m}^3$ . Inhalation at this concentration is well below the borderline range for measurable effects on human subjects.

It has been found that mixtures of sulphur dioxide and sulphuric acid exert synergistic effects on exposed animals but these effects occur at concentration levels that are much higher than those commonly found during air pollution episodes (Amdur, 34)

### (3) Hydrogen Sulphide and Mercaptans

Hydrogen sulphide, mercaptans and related sulphur compounds may on occasion constitute an odour nuisance. Hydrogen sulphide possesses the typical smell of rotten eggs. The mercaptans have a nauseating odour. The mixture of sulphur compounds may be quite unpleasant for most people in concentrations that are in excess of odour thresholds.



## E. SUMMARY

### (1) Vegetation

With reference to emissions of sulphur dioxide from large sources, the major concern is the prevention of injury to native vegetation and agricultural crops. This protection can be achieved by the establishment of limits such as 0.75 ppm of sulphur dioxide for one hour, 0.50 ppm for 3 hours and 0.30 ppm for 6 hours. For a given set of environmental factors conducive to a high degree of plant susceptibility, the relation between limiting concentration and duration of exposure to  $\text{SO}_2$  is not a simple straight line function but is an exponential relation. As the concentration is decreased, the exposure time increases exponentially until a sufficiently low concentration is attained that is non-toxic throughout the life cycle of a plant.

### (2) Animal Life

In the recorded major air pollution disasters in urban areas, animals have exhibited adverse symptoms similar to those suffered by man. Controlled laboratory tests on several animal groups have indicated that no detrimental changes could be attributed to  $\text{SO}_2$  in concentrations up to 5.5 ppm many times greater than the concentrations measured in major air pollution incidents.

### (3) Human Health

Battigelli has summarized the status of available data on the health effects of sulphur dioxide as follows: "The



search for an acceptable rationale or for reasonable evidence documenting a toxicological relevance of SO<sub>2</sub> levels, as these are encountered in urban air pollution, has thus far failed". The effect of urban air pollution on the health of exposed populations as found in acute pollution episodes and in other instances of relatively high pollutant concentrations does not appear to involve sulphur dioxide in its mechanism.





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### III LEGISLATION

#### A. Historical Outline

1. Canadian Regulations Prior to 1967
2. Federal & Provincial Regulations Subsequent  
to 1967
3. Pollution Control Legislation Alberta
4. Effectiveness of Control Methods - Alberta

#### B. Current Regulations

#### C. Future Programmes

#### D. References



### III LEGISLATION

#### A. HISTORICAL OUTLINE

##### (1) Canadian Regulations Prior to 1967

Canadian experience with the control of major air pollution problems prior to 1967 was based on regional rather than local considerations. It was customary for municipal governments to exercise control over emissions of smoke and dust from local heating and waste incineration operations, although regulation of large industrial emissions could be effectively accomplished on a regional, or provincial basis.

Beyond the provincial level in pollution control, Federal government responsibility was confined to certain aspects of a national character. It was for example, concerned with questions related to the flows of polluted air across the Canada - U.S. border. This was dealt with by the International Joint Commission established between the two countries. The Board of Transport Commissioners exercised authority under the provisions of the Canada Shipping Act in the control of smoke emission from railways or ships.

The Occupational Health Division of the Department of National Health and Welfare was the primary Federal air pollution agency. This division's activities were directed toward the provision of occupational health and air pollution advisory services, to Provincial health departments and other interested groups upon request.



The meteorological service of the Department of Transport conducted research studies on meteorological aspects of air pollution and assisted other agencies in these matters.

Other Federal agencies concerned with air pollution research included the National Research Council on the corrosive effects of air pollutants on building materials; the Department of Mines and Technical Surveys research on combustion; and the Department of Agriculture which was concerned with the effects of air pollutants on plant and animal life.

Although air pollution control was considered a matter for public health authorities and hence a provincial problem, two provinces, namely Ontario and Saskatchewan, passed separate air pollution control acts, and Quebec drafted an act in 1968. Alberta and Manitoba had specific air pollution regulations provided under their public Health Acts, while the remaining Provinces had specific regulations except for one or more clauses of the Public Health Act in cases where a health hazard could be proven. In these provinces, the municipalities could pass bylaws for the enforcement of air pollution.





(2) Federal & Provincial Pollution Control Subsequent to 1967

Canada's entry into her second century was heralded by the cries of the "concerned citizen" and the "environmentalist. United States Senator Muskie's proclamation of Earth-Day on April 22/68, soon spread the anti-pollutionist philosophy into Canada, and the environmental protection efforts of Industry, the Scientific community and certain sections of government that had been proceeding very well but highly unnoticed by the public for years, suddenly became household topics.

Government response at both the Federal and Provincial level has been rapid, well intentioned and generally effective, in spite of the problems inherent in a somewhat archaic procedure for defining local and regional responsibilities. In addition to the Federal Air Quality Act, Clean Air Acts are presently established in Alberta, Saskatchewan, Manitoba, Ontario and Newfoundland. British Columbia has just completed a series of public hearings to develop provincial standards beyond the existing municipal control. The remaining provinces have general Environmental Protection Acts for both Air and Water quality which permit them to establish objectives and control measures.

In the haste of governments (Provincial and Federal) to react to the "Environmental Crisis", it has been difficult for industry and the individual to recognize clear terms of reference and, in some cases to identify the main controlling agency. This unfortunate situation is hardly conducive to responsible citizenship, corporately or individually, and seriously inhibits a joint attack by the public and private sector upon a common problem.



It is hoped that an interdepartmental approach with industrial input will alleviate this situation, by recognizing the needs of all departments of government to guarantee environmental integrity, as well as accepting the economic-technical aspects of industry which will insure that the multiple use concept is applied in all phases of resource development.

### (3) Pollution Control Legislation in Alberta

The first legislation for the control of air pollution in Alberta was enacted in 1945 and provided a means to evaluate complaints and establish a remedy for correcting conditions where necessary. This was followed by specific legislation governing the control of dust from piles of coal and slag in 1946.

In 1955 the authority to make regulations was added, and in 1962 this was amended to include pipelines, as an item subject to control as to operations and locations. For noncompliance with the Provincial Board of Health order or with a rule or regulation for the control of air pollution, a fine could be levied, but by the terms of the Oil and Gas Conservation Act, under which all plants then operated, they were exempt from any injunction.

The first specific regulations for the control of air pollution were formulated in September of 1961. Prior to 1961, approval to construct and operate a gas plant was obtained from the Oil and Gas Conservation Board who checked with the Department of Public Health as to specific requirements before issuing a permit to construct. The main requirement was an assessment of the operators design specifications



of the proposed sulphur plant incinerator stack. Subsequent to 1961, it has been necessary to obtain provisional approval from the Department of Health before the Oil and Gas Conservation Board would entertain an application to produce and process sour gas.

A basic requirement of the 1961 Department of Health regulations was the submission of plans and specifications for all new industries to the Provincial Board of Health for approval. Any pipeline or plant which was constructed prior to, or was under construction on September 15, 1961, was exempted for a period of five years after that date, with the Board of Health empowered to reduce or extend this five year period for any specific project which it deemed in the public interest to do so.

Under the 1961 regulations, the then Air Pollution Control Branch of the Dept. of Health employed the calculated value 0.2 ppm SO<sub>2</sub> average concentration over a 30 minute period for stack design. The operating guidelines for measured concentrations in the most critical downwind areas were as listed below.

8 hour average	0.3 ppm
1 hour average	1.0 ppm
3 minute	1.5 ppm

We would observe however, that prior to this date, and as early as 1959, these values were the basis for negotiations between individual companies and the regulatory authority.

Prior to this date, the operating companies designed their sulphur incinerator stacks on the advice of consultants and other industries, working to values as low as



0.26 ppm  $\text{SO}_2$ , which even in this very early stage of the sour gas industry could match "Acceptable Standards" as presently defined by the Federal Clean Air Act objectives.

(4) Effectiveness of Control Methods - Alberta

The effect of air pollution control regulations in the Province of Alberta can be evaluated by considering the history of the gas processing industry beginning with its major expansion in the early 1950's. Until the latter years of this decade, very few sour gas processing plants existed, and the technical staffs of the two major regulatory bodies (Oil and Gas Conservation Board and Department of Public Health) were able to develop an expertise in pollution control only through the full cooperation of the operating companies.

Until 1961, design, control, and operations were essentially left up to the good judgement of the operating company, although the Provincial Board of Health still had the power to investigate a specific complaint and where necessary impose fines for violation of pollution control up to \$500 per day.

A major investigation into the Pollution Potential of the Sulphur Recovery Industry was conducted by a Scientific Advisory Board in 1963. This committee reported its findings in 1964, following a year of intensive study which stated in effect, that no pollution problem existed to cause damage. This report was referenced at the meeting of the Canadian Council of Resource Ministers in 1966.

From 1961, when the first specific regulations for the





control of pollution were formulated, until 1966, at which time all existing plants were required to conform with the new regulations, may be considered as a transition period to present day standards. For all plants built in this transition period of 1961 to 1966, and any existing plants which were modified or enlarged such that their processes were substantially changed, the regulations came into force on the date of commencement of construction or modification.

By 1966, all plants were operating under the latest Health Regulations and subsequently the industry has reflected a new awareness to the pollution problem. This awareness has been demonstrated throughout the major companies by the formulation of specific corporate policies in all matters relevant to pollution. The details of such policies vary from one company to another, however, there is one significant point common to all of them, and that is the acceptance of a community obligation to preserve air and water in an unpolluted form.

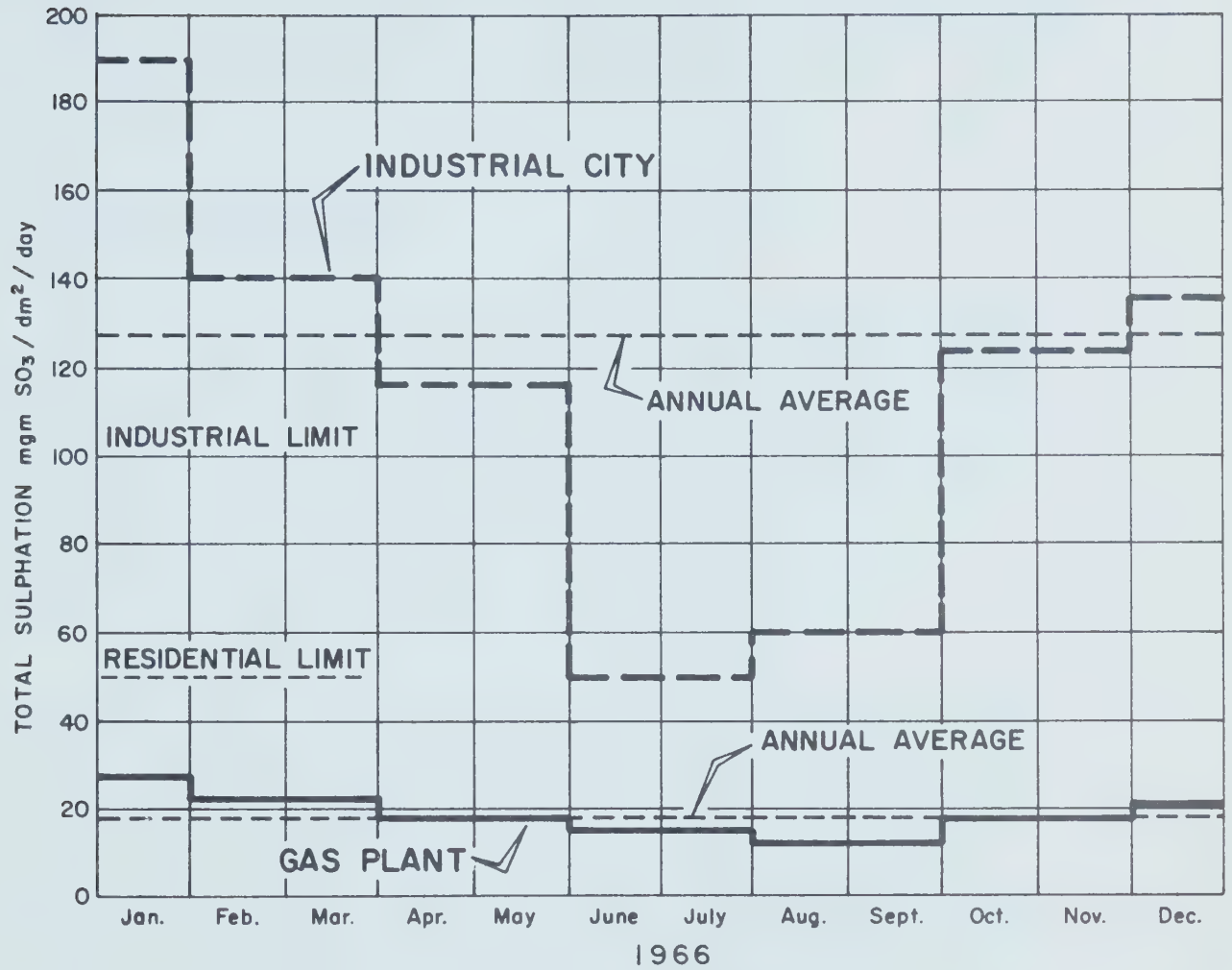
Some indication of the industry's success in its attempts to maintain minimal pollution levels may be seen in Figure III-1. The 1966 total sulphation rates for an eastern Canadian industrial city are presented in relation to those of a typical well managed sour gas processing and sulphur recovery plant in Alberta.

To date the Department of Environment has not established limits for total sulphation, but in other areas where limits have been established the acceptable rates are:

Residential	0.5 $\text{mgmSO}_3/\text{dm}^2/\text{day}$
Industrial	1.0 $\text{mgmSO}_3/\text{dm}^2/\text{day}$



## COMPARATIVE SULPHATION RATES





In this 1966 example, the gas plant area is below the recommended residential limit of 0.50 mgm. for the entire year, while 50% of the city sulphation rates exceeded the industrial allowable. Expressed in terms of annual averages, the city value of 1.26 mgms, exceeds by a factor of 7.0 the 0.18 mgm value recorded near the gas plant.

#### B. CURRENT REGULATIONS

In July 1970, the Energy Resources Conservation Board (then Oil & Gas Conservation Board) was assigned further responsibilities with respect to pollution and environmental control in the oil and gas industry. The major change resulting from this announcement was that applications for the construction and operations of gas plants were submitted to a single authority, the ERC Board.

This relieved an awkward situation wherein the Dept. of Health had refused to process applications not cleared by the Board and the Board waited for Pollution approvals by the Dept. of Health. A similar untenable situation had existed in new plant applications in forested areas wherein the Dept. of Lands & Forests required a minimum clearing to provide fire protection while the local Planning Commission wanted a minimum of one section (1 mile square) in the interests of development.

A further announcement in July 1970, outlined the respective roles of the Dept. of Health and the Oil and Gas Conservation Board under four categories:

- A. Areas of concern to both the Department and the Board.





- B. Overall Role of the Dept. of Health
- C. Overall Role of the Board
- D. Details relating to pollution control at gas processing plants.

This announcement clarified the questions of standard setting, approval granting, monitoring, reporting and enforcement, but with the publication of "Minimum Sulphur Recovery Efficiency Guidelines" by the Board in November 1971, the clarification was short lived.

The industry feels that the confusion is not so much one of jurisdiction as one of discipline, viz - Environmental Protection and Resource Utilization. The industry may not be able to challenge Environmental Protection standards in terms of immediate economics, but would be well able to do so in the matter of additional recovery and storage of commodity in considerable over supply - sulphur.

#### C. FUTURE PROGRAMMES

Progressively more stringent regulations may arise from more exacting air quality criteria in some countries to meet the pressures of increased industrialization. However, the Federal Air Quality Objectives appear more than adequate, and the Alberta regulations are similarly capable of protecting the populace at even the "nuisance level".

The top category - "Desirable", as defined by Federal Act is designed to long term goals of pristine air and to "provide an anti - degradation policy for unpolluted areas". The act does not define an unpolluted area, nor has any



authority suggested one for this jet-age of global travel.

For more than a decade, commencing with Air Pollution courses for industry personnel by the Dept. of Health, to the 1970 drafting of reporting procedures by CPA and ERCB staffs, the industry has been able to work closely with government on this common problem of Environmental Protection. Most recently, the industry has been asked to supply data to the Forestry Branch - Environment Canada to assist research studies into SO<sub>2</sub> effects on vegetation.

All future control programmes must be based on the results of research by the Academic, Government and Private sectors; and should not represent an over reaction to public pressure.



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#### IV AIR QUALITY MANAGEMENT

- A. Purpose
- B. Types of Air Pollution Control Standards
- C. Ambient Quality Vs. Emission Standards
- D. Canadian Standards
- E. Provincial Standards
- F. Comparative Air Quality Standards
- G. Ambient Air Standards for Alberta
  - (1) Present Protection
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  - (3) Future Trends
- H. References





#### IV AIR QUALITY MANAGEMENT

##### A. PURPOSE

The purpose of Air Quality Management is to insure that the primary use of the earth's air resource, to support life, is not compromised by the secondary uses which include the service of air as a transport medium, a constituent of production processes and receptacle for the waste residuals of all human activity.

Through effective air quality management, the assimilative and restorative capacity of the atmosphere will not be exceeded by the expanding population and industry.

Inherent in this statement of purpose by J. W. MacNeil in the constitutional study prepared for the Government of Canada entitled "Environmental Management", is the recognition of "assimilative capacity", in the atmosphere through the natural sulphur cycle.

##### B. TYPES OF AIR POLLUTION CONTROL STANDARDS

In general, two types of standards are employed to control air pollution in industrial and urban areas. These are emission standards and air quality standards. An emission standard establishes a limit on the quantitative rate of discharge (lbs. per hour) or concentration of a pollutant that can be emitted from a source. This emission standard limit can also be expressed in terms of the maximum permissible ground concentration at the point of impingement from the source as determined by measurement or by calculation on the basis of plume rise and diffusion theory for prevailing meteorological conditions, using specified dispersion models.



If the emission standard is expressed in terms of ground concentration limits, it can also be used as a design standard for the estimation of required stack height for a given source. In this case, the emission standard can be derived from the air quality standard.

Air quality standards are usually established on the basis of scientific criteria of cause and effect relationships between concentration level and duration of exposure to a specific pollutant of susceptible species of vegetation, animal or human health or public welfare. Other approaches to the setting of air quality standards may include the concentration levels of air quality that exist in a community on certain days of good ventilation or the conditions that existed during an earlier period when, it is believed, there were no adverse effects or the air quality conditions were tolerable by the residents of the community. Air quality standards may be adopted for an entire country or province, or different standards may be established for various areas within a jurisdiction. The "air shed" concept comprises an air quality region consisting of a geographic area which includes both the air pollution sources and the receptors within this region. Standards of air quality must be expressed in the same terms or units that are used to categorize the measurement and reporting of air quality data.

Several standards of air quality are usually employed for a major air contaminant, such as -

- (1) the annual average concentration
- (2) the 24-hour average concentration
- (3) the maximum concentration for a short period, such as 30 minutes, one hour or several hours.



The 24-hour average concentraion may be qualified by a limit, such as, that it must not be exceeded for over one percent of the days in any 3-month or in any yearly period. Similarly, the maximum concentration and its duration may be limited, such as not to be exceeded for more than the specified time in any consecutive period of hours or days.

Both emission standards and air quality standards should be accompanied by detailed description of the method of sampling and analysis for each contaminant to be employed as a reference method. This procedure has been adopted by the U. S. Environmental Protection Agency in recent publications in the Federal Register of National Air Quality and Emission Standards.

The National Research Council of Canada established in 1971 an Associate Committee on Scientific Criteria for Environmental Quality to review available information on cause and effect relationships on receptors of contaminants in air, water, soils, and other aspects, including effects of pesticides, toxic metals and physical phenomena. The work of this Associate Committee is being conducted by a Secretariat and a number of sub-committees of experts from university, industry and government. The main objective is to provide to the Canada Department of the Environment and other governmental control agencies, properly evaluated criteria which they may use to formulate quality standards.

#### C. AMBIENT STANDARDS VS. EMISSION STANDARDS

As stated previously (B. - Types of Air Pollution Control Standards) the emission standard can be derived from the air quality standard at the point of impingement. It is through this procedure, with the maximum ground level







concentration the independent variable, that Air Pollution Approvals have been issued for the sulphur recovery plants in the past. The ambient air quality standard protects the environment and is particularly suited to the Sour Gas Industry which is made up of isolated, essentially single point sources.

For ease of enforcement and control, Emission Standards may well be more applicable in situations of intensive, multiple sources such as domestic heating with sulphur bearing fuels, but even in this application, the emission standard should be based on an ambient air quality with computed dispersion rates for the multitude of sources.

Sour Gas Processing and Sulphur Recovery plants constitute the ultimate step in the elimination of significant groups of multiple sources, by recovering and processing the many small, and often uneconomic quantities of  $H_2S$  containing gases associated with crude oil production. Flaring operations could not be controlled by emission standards where the quantity of gas is a function of the oil production rate, and the concentration an accident of geologic history.

In the rare case of potentially merging plumes from adjacent gas plants, the ambient air quality approach can dictate some method of plant production prorationing combined with changes in dispersion through temporarily elevated stack emission temperatures to meet the existing meteorological conditions.

#### D. CANADIAN STANDARDS

On October 21, 1971, the Honourable Jack Davis, Minister of the Environment, announced proposed National Air Quality



Objectives for five major air pollutants: - sulphur dioxide, particulate matter, carbon monoxide, photochemical oxidants and hydrocarbons.

Mr. Davis noted that the Federal Clean Air Act was unique in that it called for three levels of air quality objectives - "desirable", "acceptable", and "tolerable" - for each major air pollutant, but his announcement concerned only the first two levels. Air quality objectives for nitrogen oxides, the sixth major air pollutant, are also under consideration and are expected to be announced shortly.

Under the Clean Air Act, the National Air Quality Objectives are designed to protect public health and welfare by setting limits on levels of pollution in the air. The maximum acceptable level corresponds in concept to the secondary air quality standards recently announced by the United States and to air quality objectives in use by some provinces in Canada. This level is intended to provide adequate protection against effects on soil, water, vegetation, materials, animals, visibility, personal comfort and well-being. It represents the realistic objective today for all parts of Canada. When this level is exceeded, control action by a regulatory agency is indicated.

The maximum desirable level defines the long term goal for air quality and provides a basis for an anti-degradation policy for the unpolluted parts of the country and for the continuing development of control technology. Maximum tolerable levels, to be announced at a later date, are intended to indicate the onset of an "imminent danger" requiring immediate abatement action. Air pollution episodes which sometimes result when pollutants accumulate during adverse weather conditions would fall within this category.



The proposed air quality objectives announced were developed in consultation with provincial officials and are based on the recommendations of a Federal-Provincial Committee of experts. Mr. Davis noted that the excellent cooperation between federal and provincial authorities was an indication of the very real desire of both levels of government to come to grips with the problems of air pollution.

The proposed maximum acceptable levels and maximum desirable levels follow:

#### Maximum Acceptable Levels

##### Sulphur Dioxide

- 60 micrograms per cubic meter (0.02 ppm) annual arithmetic mean
- 300 micrograms per cubic meter (0.11 ppm) as a maximum 24-hour concentration
- 900 micrograms per cubic meter (0.34 ppm) as a maximum one-hour concentration

##### Particulate Matter

- 70 micrograms per cubic meter annual geometric mean
- 120 micrograms per cubic meter as a maximum 24-hour concentration

##### Carbon Monoxide

- 15 milligrams per cubic meter (13 ppm) as a maximum eight-hour
- 35 milligrams per cubic meter (30 ppm) as a maximum one-hour

##### Photochemical Oxidants

- 30 micrograms per cubic meter (0.015 ppm) annual arithmetic mean





- 50 micrograms per cubic meter (0.025 ppm) as a maximum 24-hour concentration
- 160 micrograms per cubic meter (0.08 ppm) as a maximum one-hour concentration

#### Hydrocarbons

- 160 micrograms per cubic meter (0.24 ppm) as a maximum three-hour concentration

### Maximum Desirable Levels

#### Sulphur Dioxide

- 30 micrograms per cubic meter (0.01 ppm) annual arithmetic mean
- 150 micrograms per cubic meter (0.06 ppm) as a maximum 24-hour concentration
- 450 micrograms per cubic meter (0.17 ppm) as a maximum one-hour concentration

#### Particulate Matter

- 60 micrograms per cubic meter annual geometric mean

#### Carbon Monoxide

- 6 milligrams per cubic meter (5 ppm) as a maximum eight-hour concentration
- 15 milligrams per cubic meter (13 ppm) as a maximum one-hour concentration

#### Photochemical Oxidants

- 20 micrograms per cubic meter (0.01 ppm) annual arithmetic mean
- 30 micrograms per cubic meter (0.015 ppm) as a maximum 24-hour concentration
- 100 micrograms per cubic meter (0.05 ppm) as a maximum one-hour concentration





#### E. PROVINCIAL STANDARDS

At the provincial level, the most comprehensive standards are those established by Ontario and Alberta. Other provinces of Canada have not adopted such standards as yet or have only minimal requirements either at the provincial level or within metropolitan jurisdictions. The Alberta emission and ambient air quality standards are included in the status report on the hearing. Values adopted by these two provinces for the same contaminants are comparable in general. The Ontario criteria for desirable air quality (Schedule 2) for sulphur dioxide is 0.25 ppm for one hour, 0.10 ppm average for 24 hours and 0.02 ppm average for one year. In Alberta the comparable levels are 0.30 for one hour and 0.10 for 24 hours. For hydrogen sulphide, the Ontario desirable limit is 0.02 ppm for one hour, whereas in Alberta the specified limit is 0.03 ppm for one hour and 0.005 ppm for 24 hours.

#### F. COMPARATIVE AIR QUALITY STANDARDS

The United States National Ambient Air Quality Standards, published in the Federal Register of April 30, 1971 for six major contaminants, are set forth in Table IV-1. The U. S. standards are of two types, primary and secondary. Primary standards are based on criteria regarding effects of the pollutants on human health, whereas the secondary standards include effects on other aspects of public welfare, i.e., social, economic, etc. In this connection, it is of interest to note that the U. S. secondary standard for sulphur dioxide permits a maximum concentration level of 0.50 ppm for 3 hours. This is much more realistic as regards effects on vegetation - a more sensitive receptor than man or animals - than the Canadian proposed federal standards or those of either Alberta or Ontario.



TABLE IV-1

U.S. Federal Ambient Air Quality Standards  
(Federal Register, Vol. 36, No. 84, April 30, 1971)

Substance	Primary Standard		Secondary Standard	
	micrograms per m <sup>3</sup>	p.p.m. (by vol.)	micrograms per m <sup>3</sup>	p.p.m. (by vol.)
Sulphur oxides (measured as SO <sub>2</sub> ) --				
Annual arithmetic mean	80	0.03	60	0.02
Maximum 24-hr. conc.	365	0.14	260	0.10
Max. 3-hr. conc.	-	-	1,300	0.50
Particulate Matter --				
Annual geometric mean	75		60	
Maximum 24-hr. conc.	260		150	
Carbon Monoxide --				
Maximum 8-hr. conc.	10 mg/m <sup>3</sup>	9	10 mg/m <sup>3</sup>	9
Maximum 1-hr. conc.	40 mg/m <sup>3</sup>	35	40 mg/m <sup>3</sup>	35
Photochemical Oxidants --				
Maximum 1-hr. conc.	160	0.08	160	0.08
Hydrocarbons (measured as carbon and corrected for methane) --				
Max. 3-hr. conc.(6-9a.m.)	160	0.24	160	0.24
Nitrogen dioxide --				
Annual arithmetic mean	100	0.05	100	0.05

Note: Measurements of air quality are corrected to a reference temperature of 25°C and pressure of 760 Torr (1013.2 millibars). Maximum concentrations must not be exceeded more than once per year.



A comparison of U. S., Canada and Ontario standards for five major air pollutants is presented in Table IV-2. There are considerable discrepancies between the U. S. and Canadian standards. Those published by the U. S. Environmental Protection Agency are accompanied by a detailed description of the methods of air sampling and analysis that must be used to measure the required concentration levels of air contaminants. Such methods are a vital part of any standards because analytical methods may vary considerably as to range and sensitivity, precision, accuracy, specificity and interferences from other co-existing substances in the sample. No methods of analysis are given for the Canadian and Ontario standards. This is a serious omission.

Standards proposed for Canada are unrealistic as to potential effects on receptors. Levels for SO<sub>2</sub> and particulate matter are much too low. The annual and 24-hour maximum levels for photochemical oxidants are equivalent to or less than the natural background concentrations of ozone or oxidants prevailing in rural areas due to electrical discharges or diffusion to the lower atmosphere from the stratosphere.

Annual geometric means for particulate matter can be exceeded by natural background contamination from windblown soil, vegetation and other particles such as pollen, spores, etc. Hydrocarbons emitted from forests in combination with natural evolution of oxides of nitrogen will yield higher concentrations of photochemical oxidants than those given in the Canadian standards for annual and 24-hour means.

A maximum SO<sub>2</sub> level of 0.50 ppm for 3 hours (U. S. Standard) is much more appropriate than the Canadian one-hour level. None of the standards for particulate matter specifies





TABLE IV-2

Comparative Ambient Air Quality Standards

Substance	United States		Canada		Ontario
	Primary	Secondary	Maximum Acceptable	Maximum Desirable	Desirable Schedule 2
Sulphur Dioxide -	Parts per million by volume -				
Annual Arithmetic mean	0.03	0.02	0.02	0.01	0.02
Max. 24-hr. conc.	0.14	0.10	0.11	0.06	0.10
Max. 3-hr. conc.	-	0.50	-	-	
Max. 1-hr. conc.	-	-	0.34	0.17	0.25
Particulate Matter -	Micrograms per cubic meter -				
Annual geometric mean	75	60	70	60	60
Max. 24-hr. conc.	260	150	120	-	90
Carbon Monoxide -	Parts per million by volume -				
Maximum 8-hr. conc.	9	9	13	5	15
Maximum 1-hr. conc.	35	35	30	13	40
Average 24-hr. conc.	-	-	-	-	8
Photochemical Oxidants -	Parts per million by volume -				
Annual arithmetic mean	-	-	0.015	0.01	-
Max. 24-hr. conc.	-	-	0.025	0.015	0.03
Max. 1-hr. conc.	0.08	0.08	0.08	0.05	0.10
Hydrocarbons -	Parts per million by volume -				
Max. 3-hr. conc., U.S. (measured as carbon and corrected for methane)	0.24	0.24	-	-	-
Max. 3-hr. (no method specified)			0.24		



the particle size range or chemical nature of the material. It is well known that the respirable range excludes particles larger than 7.5 microns in diameter. The usual method of sampling for particulates involves collection of a 24-hour sample by filtration of a measured volume of air. This collects material ranging from sub-micron size to "rocks" of 40 to 100 micron diameter. Mass concentrations without particle size distribution and chemical composition is meaningless as to potential effects on receptors.

The State of California was the first government jurisdiction to adopt ambient air quality standards in North America (State of California, Department of Public Health, 1959 and 1962). Their published Air Quality Standards with Footnotes are presented in Table IV-3. The "adverse level" for sulphur dioxide at 1.0 ppm for 1 hour and 0.30 ppm for 8 hours, on the basis of plant damage, is still the most realistic standard in relation to known criteria for the most susceptible species of vegetation. It is probable that the California limits of air quality will be superseded by the U. S. Federal standards.

Limits of allowable concentrations of atmospheric pollutants established by the U. S. S. R. are presented in Table IV-4. Two limits have been adopted for each pollutant; a single maximum concentration, usually for a duration of about 20 minutes, and a 24-hour average concentration, in units of milligrams per  $\text{m}^3$  of air. For  $\text{SO}_2$  the maximum concentration in ppm by volume is only 0.19 and the 24-hour average, 0.057 ppm (at  $25^\circ\text{C}$  and 760 Torr). For hydrogen sulphide, the maximum level is equivalent to 0.02 ppm and the 24-hour average to 0.007 ppm. In general, the Russian limits are lower than those of any other nation in the world. However, a review of actual air quality data in Russian cities and industrial areas indicates that their standards have not



TABLE IV-3

## State of California Standards for Ambient Air Quality

POLLUTANT	"ADVERSE" LEVEL	"SERIOUS" LEVEL	"EMERGENCY" LEVEL
	Level at which there will be sensory irritation, damage to vegetation, reduction in visibility or similar effects.	Level at which there will be alteration of bodily function or which is likely to lead to chronic disease.	Level at which it is likely that acute sickness or death in sensitive groups of persons will occur.
Oxidant	"Oxidant Index"	Not applicable	Not applicable
Ozone	0.15 ppm for 1 hr by the potassium iodide method (eye irritation, plant damage and visibility reduction)	Footnote 1	Footnote 2
Nitrogen Dioxide		Footnote 3	Footnote 3
Hydrocarbons		Footnote 4	Footnote 4
Photochemical Aerosols		Not applicable	Not applicable
Carcinogens	Not applicable	Footnote 5	Not applicable
Sulphur Dioxide	1 ppm for 1 hr or 0.3 ppm for 8 hrs (plant damage)	5 ppm for 1 hr (bronchoconstriction in human subjects)	10 ppm for 1 hr (severe distress in human subjects)
Sulphuric Acid	Footnote 6	Footnote 6	Footnote 7
Carbon Monoxide	Not applicable	30 ppm for 8 hrs or 120 ppm for 1 hr (interference with oxygen transport by blood)	Footnote 8
Lead	Not applicable	Footnote 9	Footnote 9
Ethylene	Footnote 10 0.5 ppm for 1 hr or 0.1 ppm for 8 hrs (damage to vegetation)	Not applicable	Not applicable
Particulates	Sufficient to reduce visibility to less than 3 miles when relative humidity is less than 70%	Not applicable	Not applicable
Hydrogen Sulphide	0.1 ppm for 1 hr (sensory irritation)	5 ppm may interfere with appetite in sensitive groups	50-100 ppm for 1 hr may cause conjunctivitis and irritation
Hydrogen Fluoride	Footnote 11	Footnote 11	Not applicable

## Footnotes to Table 3

1. Ozone, at 1 ppm for 8 hrs daily for about a year, has produced bronchiolitis and fibrositis in rodents (Stokinger, H.E., Wagner, W.D., and Dobrogorski, O.J. A.M.A. Archives of Industrial Health, 16:514,





## FOOTNOTES TO TABLE IV-3 (Continued..)

1957). Extrapolation of these data to man is difficult. Functional impairment data have been reported by Clamann and Bancroft (Clamann, H.G., and Bancroft, R.W. *Advances in Chemistry*, No. 21, pp. 352-359, 1959); at 1.25 ppm some effect is observed on residual volume and diffusing capacity. The variability of the tests was not reported. Additional data would be needed before a standard is set.

2. A value of 2.0 ppm of ozone for 1 hr may produce serious interference with function in healthy persons, and the assumption is made that this might cause acute illness in sensitive persons. (Clamann, H.G., op. cit.).
3. Five ppm of nitrogen dioxide for 8 hrs will produce decreased pulmonary function in animals. Slightly more may produce pulmonary fibrosis (Stokinger, personal communication); nitrogen dioxide from air pollution exposures is usually combined with nitric oxide and ozone. More data on human exposures will be needed prior to setting a standard.
4. Hydrocarbons are a group of substances most of which, normally, are toxic only at concentrations in the order of several hundred parts per million. However, a number of hydrocarbons can react photochemically at very low concentrations to produce irritating and toxic substances. Because of the large number of hydrocarbons involved, the complexity of the photochemical reactions, and the reactivity of other compounds such as nitrogen dioxide and ozone, it is not yet possible to establish "serious" and "emergency" levels for hydrocarbons. From the public health standpoint, the concentration of those hydrocarbons which react photochemically should be maintained at or below the level associated with the oxidant index defined in the "adverse" standard.
5. Carcinogens include a few organic compounds such as some polycyclic hydrocarbons, and some metals such as arsenic and chromium. Studies on effects of such substances are currently under way, but there are not sufficient data, at present, to set standards. In the meantime, it is recommended that concentrations of carcinogens in air should be kept as low as possible.
6. A sulphuric acid mist level of  $1 \text{ mg/m}^3$  with an average particle size of one micron will produce a respiratory response in man. (Amdur, M.O., Silverman, L., and Drinker, P. *Archives of Industrial Hygiene and Occupational Medicine*, 6:305, 1952). It is not possible to generalize from this for all air pollution conditions, because under natural conditions, particle size will vary. Only with large droplets would sensory irritation be produced without other physiological effects.
7. A level of  $5 \text{ mg/m}^3$  of sulphuric acid mist for a few minutes produces coughing and irritation in normal individuals (Amdur, M.O., Silverman, L., and Drinker, P. op. cit.). Presumably, it could cause acute illness in sensitive groups of persons in a period of 1 hr.
8. Given certain assumptions concerning ventilatory rates, acute sickness might result from a carbon monoxide level of 240 ppm for 1 hr in sensitive groups because of inactivation of 10% of the body's hemoglobin. In any event it is clear that when a population exposure limit has been set for carbon monoxide, because of exposures from other sources, community air pollution standards should be based on some fraction of this limit.
9. It is clear that lead levels should be set on the basis of average values for long periods. While data are abundant concerning human response to eight-hours-a-day, five-days-a-week exposure, data are insufficient for the effects of the continuous exposure inherent in community air pollution. While laboratory studies will be pursued with vigor, it becomes very important that local agencies collect data on existing lead levels. Since lead exposures are from multiple sources, community air pollution standards should be based on a portion of the total limit for population exposure.
10. Ethylene causes severe damage to vegetation. Ornamental plants are severely injured by exposures from 0.2 to 0.5 ppm. Tomatoes and fruit are adversely affected at similar levels.
11. Hydrogen fluoride and other airborne fluorides settle upon and some are absorbed into vegetation. When forage crops containing 30-50 ppm of fluoride measured on a dry weight basis are regularly consumed over a long period, the teeth and bones of cattle may show changes, depending upon age, nutritional factors and the form of fluoride ingested. Such changes may or may not have any economic effect. Fluorides at these levels do not necessarily cause injury to the forage plants themselves. The irritating properties of hydrogen fluoride in experimental human exposure have been manifested by desquamation of the skin, at concentrations of 2-5 ppm. Mucous membrane irritation also occurs from hydrogen fluorides but quantitative data are not adequate to support a standard.





TABLE IV-4

Russian (U.S.S.R.) Limits of Allowable Concentrations  
of Atmospheric Pollutants

	Limits of allowable concentrations in mg/m <sup>3</sup>	
	single maximum	average daily (24 hrs)
Sulphuric acid aerosol	0.30	0.10
Sulphur dioxide	0.50	0.15
Hydrogen sulphide	0.030	0.010
Hydrogen sulphide in combination with petroleum gas	0.015	0.005
Phenol	0.30	0.10
Benzene	2.4	0.8
Fluorine compounds	0.03	0.01
Carbon monoxide	6.0	1.0
Hydrogen chloride	0.05	0.015
Dust (non toxic)	0.50	0.15
Fluorine and its compounds (as .F)	0.03	0.01
Nitrogen oxides	0.30	0.10
Chlorine	0.10	0.03
Lead	-	0.0007



been implemented as yet.

A number of West German air quality standards is given in Table IV-5. In the case of sulphur dioxide, a peak level of 0.30 ppm is the maximum permissible concentration for three half-hour periods daily in excess over a steady value of 0.15 ppm. Under similar terms, the corresponding peak value for hydrogen sulphide is 0.20 ppm and the steady value 0.10 ppm.

Japan has adopted an air quality standard for sulphur dioxide of 0.20 ppm for 3 hours. In the Netherlands, the SO<sub>2</sub> standard varies over the average range for 24 hours from 0.05 to 0.18 ppm, depending upon the nature of the area in relation to concentration of industry and population.

An excellent review of air pollution standards that covers the practice in many countries of the world has been presented by A. C. Stern in Chapter 51 of Volume III of "Air Pollution", Second Edition, Academic Press, 1968. In Canada, the Associate Committee of the National Research Council has not accepted the conclusions reached in the Air Quality Criteria Documents published by the National Air Pollution Control Office of the United States (EPA), believing that many of the findings reported in the literature by scientific investigators have not been properly interpreted. It is believed that more accurate criteria on which to base standards will become available to Canada as a result of these NRC studies.

#### G. AMBIENT AIR STANDARDS FOR ALBERTA

##### (1) Present Protection

In Section II, an effort was made to indicate the limits



TABLE IV-5

West German Air Quality Standards

(VDI - Kommission Reinholtang der Luft)

	Maximum permissible concentration	
	Steady Value (as half-hour average)	Peak Value <sup>(a)</sup> (as half-hour average) <sup>(b)</sup>
	<u>ppm</u>	<u>ppm</u>
Sulphur Dioxide	0.15	0.30
Oxides of Nitrogen	0.5	1.0
Chlorine	0.1	0.5
Hydrogen Sulphide	0.1	0.2

(a) Permissible excess over steady value.

(b) Not to be exceeded more than three half-hour periods daily.





of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  that can be tolerated by the environment. Now let us examine the limits as set by the Alberta Department of the Environment on these compounds. Table IV-6 gives the Alberta Ambient Air Quality Standards for  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and several other pollutants. The one hour average concentrations limit for  $\text{SO}_2$  is 0.30 ppm and for  $\text{H}_2\text{S}$  it is 0.030 ppm. In the case of  $\text{SO}_2$  previous discussion showed that a concentration of 0.30 ppm presented no detrimental effects on the most sensitive plants, when exposed to such concentrations for four hours per day for a month. Thus the limit of 0.30 ppm for one hour for  $\text{SO}_2$  is more than adequate to protect vegetation, animals and humans. Similarly the limit for  $\text{H}_2\text{S}$  is well below any concentrations that would harm the vegetation or humans. The twenty-four hour limits of 0.10 ppm and 0.005 ppm respectively for  $\text{SO}_2$  and  $\text{H}_2\text{S}$  currently in effect in Alberta are also well below those that studies shows would cause adverse effects.

The Ambient Air Quality Standards published by the Department of the Environment in Alberta are designed to "protect the health and welfare of all citizens and maintain the quality of the Province's air resource and prevent insofar as possible, deleterious effects to animals, plants and property".

Further to the Ambient Air Quality Standards, the Report has provided a schedule of "Maximum Calculated Ground-level Concentration Standards". A comparison of these standards, together with those recommended under the Federal Governments Clean Air Act are shown in Table IV-7. Significantly, the Federal (Canada) and Alberta standards include "welfare" as their objectives, which implies that both damage and nuisance levels have been fully considered. Further the "welfare" objective provides a safety factor beyond the critical levels for plant damage.



TABLE IV-6

## AMBIENT AIR QUALITY STANDARDS

POLLUTANT	CONCENTRATION UNIT	AVERAGE CONCENTRATION FOR APPLICABLE TIME PERIOD		METHOD OF MEASUREMENT
		1 HR.	24 HR.	
1 FLUORIDES (as HF)	ppm. (vol.)		.0040	Spectrophotometry
	mg./m <sup>3</sup>		.0033	
FLUORIDES in forage for livestock (dry wt. as F)	ppm. (wt.)		35.0	Gravimetry
	mg./l		35.0	
2 TOTAL OXIDANTS (as O <sub>3</sub> )	ppm. (vol.)	.15	.10	Spectrophotometry
	mg./m <sup>3</sup>	.29	.20	
3 TOTAL OXIDES OF NITROGEN (as NO <sub>2</sub> )	ppm. (vol.)	.30	.10	Spectrophotometry
	mg./m <sup>3</sup>	.56	.19	
4 CARBON MONOXIDE (CO)	ppm. (vol.)	60.0	8 hour average 15.0 ppm. (vol.) (17.2 mg./m <sup>3</sup> )	Infrared Spectrophotometry*
	mg./m <sup>3</sup>	68.7		
5 HYDROGEN SULFIDE (H <sub>2</sub> S)	ppm. (vol.)	.030	.005	Light transmittance or reflectance
	mg./m <sup>3</sup>	.042	.007	
6 SULFUR DIOXIDE (SO <sub>2</sub> )	ppm. (vol.)	.30	.10	Conductivity
	mg./m <sup>3</sup>	.79	.26	
7 SOILING INDEX	coh	90% of average readings per month < 1.0	Annual Average < .45	Light transmittance or reflectance



TABLE IV-7

SULPHUR DIOXIDE (PPM)

FEDERAL AIR QUALITY  
OBJECTIVES

---

ALBERTA  
AMBIENT STANDARDS DESIGN  
(MEASURED) (CALCULATED)

---

(a) TOLERABLE

(b) ACCEPTABLE

1/2 hour	----		0.2
1 hour	0.34	0.30	
24 hours	0.11	0.10	
Annual	0.02		

(c) DESIRABLE

1 hour	0.17
24 hours	0.06
Annual	0.01



The "Maximum calculated groundlevel concentration standards" provide adequate safe design criteria, for sulphur plant stack heights. Summarily, the Alberta standards allow for two orders of safety beyond the levels where plant damage could occur. The absence of SO<sub>2</sub> vegetation damage downwind of gas plants in Alberta verifies the cautious approach used by the authorities to date in granting approvals.

## (2) Alberta Standards in Light of Others

Ambient Air Quality Standards established by various Government agencies in the United States and Canada are listed in Table IV-8.

It can be noted that there are considerable discrepancies between the Canadian proposed objectives and the U. S. standards. A maximum acceptable limit of 0.34 for one hour is unrealistic in terms of known criteria for sulphur dioxide effects on sensitive plant species. This type of exposure is harmless and very much below the exposure threshold for minimum leaf injury. The U. S. (EPA) secondary standard of 0.50 ppm for 3 hours <sup>(26)</sup> is one that relates to effects on public welfare (including vegetation), comparable to the Canadian definition of a "desirable" level. It is a much more realistic limit for protection of plant life. In Alberta, the SO<sub>2</sub> standard is set at 0.30 ppm for one hour and 0.10 for 24 hours.

Maximum 24-hour concentrations at all the levels indicated above are meaningless regarding vegetation, unless they include several hours of peaks greater than 0.50 ppm. On the basis of both experimental studies and field experience, 24-hour exposures in the range of 0.14





TABLE IV-8

Comparative Ambient Air Quality Standards for Sulphur Dioxide

Maximum Exposure Limit	State of California Adverse level ppm	U. S. Environmental Protection Agency		Canada		Ontario Desirable Schedule 2 ppm	Alberta
		Primary ppm	Secondary ppm	Max. Acceptable ppm	Max. Desirable ppm		
One hour	1.0	--	--	0.34	0.17	0.25	0.30
3 hours	--	--	0.50	--	--	--	--
8 hours	0.30	--	--	--	--	--	--
24 hours	--	0.14	0.10	0.11	0.06	0.10	0.10
Annual Arithmetic mean	--	0.03	0.02	0.02	0.01	0.02	--



to 0.10 ppm are very much below threshold limits, since normal crop plants can be grown in a continuous atmosphere at such levels.

With reference to emissions of sulphur dioxide from large sources, the major concern is the prevention of injury to native vegetation and agricultural crops. This protection can be achieved by the establishment of limits such as 0.75 ppm of sulphur dioxide for one hour, 0.50 ppm for 3 hours and 0.30 ppm for 6 hours. For a given set of environmental factors conducive to a high degree of plant susceptibility, the relation between limiting concentration and duration of exposure to  $\text{SO}_2$  is not a simple straight line function but is an exponential relation. As the concentration is decreased, the exposure time increases exponentially until a sufficiently low concentration is attained that is non-toxic throughout the life cycle of a plant.

### (3) Future Trends

The problems with  $\text{H}_2\text{S}$  and  $\text{SO}_2$  around sour gas operations can be classified into two categories: as potentially harmful to growth and health, or as a nuisance due to bad odours. It was shown that the Alberta Ambient Air Quality Standards currently in effect are already more than adequate to protect the health of vegetation, animals and humans. The main source of  $\text{SO}_2$  is the sulphur plant stack. Reducing  $\text{SO}_2$  emissions from this source will have no bearing on the other problem, namely, odours around sour gas operations. As mentioned, the odours are due to hydrogen sulphide and mercaptans, and none of these compounds originate from the sulphur plant stack. Thus enforcing a more stringent standard with regard to  $\text{SO}_2$  will have no bearing on the problem of odours, as the threshold odour concentration of



SO<sub>2</sub> is 0.47 ppm, which is higher than the one hour SO<sub>2</sub> limit of 0.30 ppm. Since the current Alberta Ambient Air Quality Standards are already more than adequate for the protection of the environment, a further restriction would be analogous to imposing a 30 m.p.h. speed limit on the No. 2 highway between Calgary and Edmonton, in order to improve traffic safety.

In Alberta, The Department of the Environment sets the Ambient Air Quality Standards, and the Energy Resources Conservation Board monitors and enforces these standards. However, under current practice, the Board has superimposed its own sulphur plant stack emission standards, which are in many cases more stringent than the Air Quality Standards. It is strongly felt by industry that the approach to this overall problem of ambient air quality should be through the Department of the Environment setting the Ambient Air Quality Standards, and this should be sole criterion for monitoring the performance of sulphur plants. Thus the performance of the sulphur plant operation should be judged on the SO<sub>2</sub> content of the surrounding air. The present system of two agencies of the government setting different regulations on SO<sub>2</sub> levels is not a desirable situation for the operation of sulphur plants.





## V   STACK DESIGN

- A.   Predicted Ground Level Concentration
- B.   Analytical Models
- C.   Numerical Models
- D.   Variability of Plume Rise Estimates
- E.   References



## V STACK DESIGN

### A. PREDICTED GROUND LEVEL CONCENTRATION

Sulphur plant waste gases are emitted to the atmosphere through incinerator stacks designed for maximum ground level concentrations of sulphur dioxide to be within the half-hour concentration standard applicable to the area. The design calculation principles currently utilized by the Energy Resources Conservation Board are the analytical type models of Sutton and Pasquill (Dept. Health Handbook)<sup>(1)</sup>. Industry experience indicates that stacks designed by these methods provide more than adequate environmental protection at ground level by virtue of measured SO<sub>2</sub> ground level concentrations being less than ambient air standards 99% of the time<sup>(2)</sup>. It is also recognized that other factors affecting low ground level concentrations could be plant gas throughput volumes less than design maximums and because stack design criteria of critical atmospheric wind speed is experienced only a minor portion of the time. Incidents of ground level concentrations exceeding standards to occur on occasion because of topographical or meteorological phenomena. The Topographical exceptions may be precluded in future with improved air quality modelling techniques while the meteorological exceptions, because of unpredictable intensity and occurrence currently are regarded as impractical to prevent. Despite these phenomena it is contended there is no conclusive evidence of vegetation or animal damage in this province resulting from sulphur plant stack emissions. Concern in the past over "nuisance" odors are believed primarily to have resulted from problems in field well operations. These operations have been materially improved during recent years with an accompanying reduction of field area resident complaints.



The CPA agrees with the statement of the ECA Situation Report that while, "the formula used to establish a proper stack height for a pollution emission rate have a certain amount of physical justification, they are basically just useful approximations". However recognition must be given to the predicament of obtaining more data and utilizing involved techniques at considerable cost for those cases where there is only a marginal improvement in prediction capability. The present Sutton and Pasquill methods have been found to be appropriate generally for level terrain conditions but may provide erroneous predictions for significant topographic features. Undoubtedly as technology develops in this area it will be applied by industry and accepted by regulatory bodies.

#### B. ANALYTICAL MODELS

Bibbero (3) States "...the primary question asked of a mathematical model (is): "What will be the pollutant concentrations at any point in the air quality region, given all the data on sources and meteorological conditions. In theory, a complete answer to this question can be given only be continuously tracking the pollutants emitted from individual sources and computing the concentration of each species at every point as they are transported by wind, spread by diffusion, mixed by turbulence, and reflected or channeled by surfaces such as ground or valleys. The basic consideration of mass continuity in fluid dynamics leads to complex vector equations that describe the time varying changes in the concentration field. The problem is much like that of trying to describe the changing intensity of a soluble dye at every point after it is dropped into a swirling, turbulent brook, except that (in air quality modelling) we must also account for the chemical decay of



each species with time and their reactions to each other."

The equation basic to modelling<sup>(4)</sup> after a number of simplifications which neglect the small rates of molecular diffusion as compared with the much greater turbulent eddy diffusion (E) coefficients, results in an expression of the following form:

(1)

$$\frac{\partial C}{\partial t} + \bar{U} \cdot \nabla C = \nabla \cdot E \nabla C + q + q_{ga} + R$$

Where:

- C Pollutant concentration
- E Eddy diffusivity with components  $E_x$ ,  $E_y$  and  $E_z$  in the x, y and z directions, respectively
- t time
- R Rate of disappearance of pollutant due to reaction
- $\bar{U}$  Time averaged air velocity vector consisting of vectors u, v and w in the x, y and z directions, respectively
- q. pollutant source rate
- $q_{ga}$  Pollutant ground adsorption rate

This equation assumes that the air density does not change with space or time.

The exact solution of (1) is difficult to implement because of the serious problems in defining the diffusion coefficients E, and the non linear nature of the chemical reaction term R. The diffusion coefficient E is a function of the size and the velocities of the turbulent eddies which in turn depend on many factors and interactions and as a result become very complicated functions of their positions in the field.





If the chemical reaction and ground adsorption terms are ignored and the magnitude of the diffusion coefficients is considered known (may be determined from the field data), then the exact solution for the steady state version of equation (1) can be obtained. The wind velocity and diffusivity may be either assumed constant or allowed to vary as a known power law function.

Sutton<sup>(5)</sup> solves for pollutant concentration considering height dependent diffusivity and velocity and concludes that use of velocity given by one-seventh power law and eddy diffusivity given by six-sevenths power law, gives ground concentrations in good agreement with observations of smoke dissipation from a continuous line source.

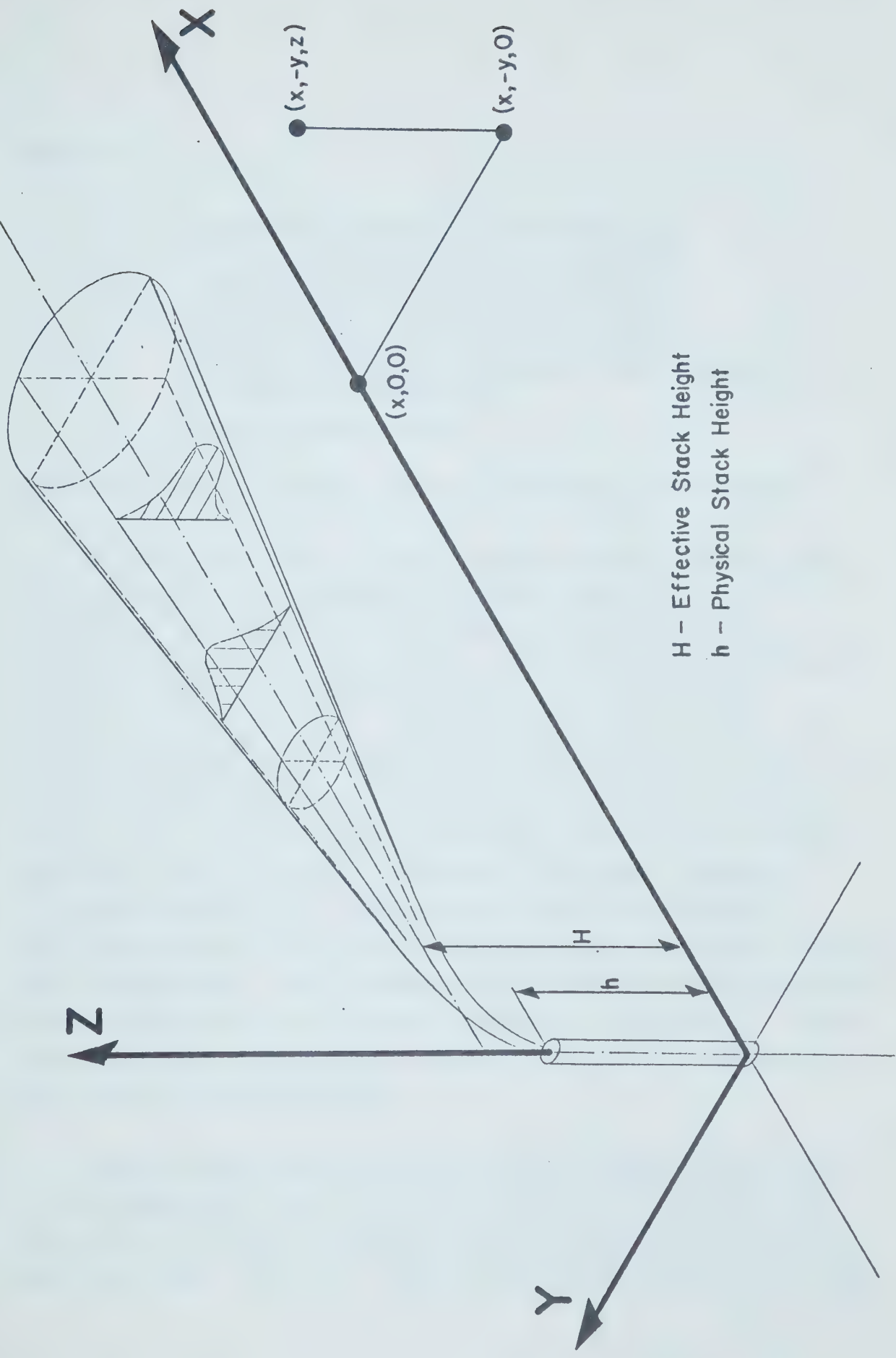
Rather than employing a purely analytical solution, useful attempts (such as one due to Pasquill<sup>(6)</sup>) have been made to utilize the statistical properties of turbulence. The most popular scheme is to assume that the plume on a single species of effluent (neglecting any chemical reaction) from each source spreads out randomly as it is blown downwind (Gaussian Plume Model). Thus, the pollutant concentration along any axis across the plume's cross section is distributed according to the familiar Gaussian or bell shaped curve (see Figure V-1). A continuous point source is located at  $x=y=z=0$ . Dispersion in the x-direction downwind of stack (or source) is ignored and the mean wind speed is assumed constant in time.

The pollutant concentration at any point is then given the following relationship for wind in the x-direction:

$$C = \frac{q}{2\pi\sigma_y\sigma_z u} e^{-\frac{y^2}{2\sigma_y^2} - \frac{z^2}{2\sigma_z^2}}$$



CO-ORDINATE SYSTEM SHOWING GAUSSIAN DISTRIBUTION  
IN HORIZONTAL AND VERTICAL DIRECTION



H - Effective Stack Height  
h - Physical Stack Height

Figure V-1



Where:

$\sigma_y$	Standard deviation of horizontal gas concentration distribution in plume
$\sigma_z$	Standard deviation of vertical gas concentration distribution in plume
y	Lateral distance from vertical plane through the stack (or source) and parallel to mean wind direction.
z	Height above ground

and other symbols are the same as previously presented.

It is noted that the previous problem of determining the diffusion coefficients E has been offset by a similar problem in the Gaussian plume model of evaluating new statistical variables  $\sigma_y$  and  $\sigma_z$ . A number of field studies however, have been conducted resulting in expressions capable of defining the standard deviations in terms of diffusion parameters. The diffusion parameters in turn depend on stability, mixing depth as well as the gustiness of the wind. These factors, of course, vary with terrain. Although rather extensive evaluation has been conducted in Brookhaven National Laboratories where the ground is flat and wooded and in the rolling country of Porten, England, the terminology used to describe stability and the numerical values obtained have not been in perfect agreement<sup>(7)</sup>. Thus there is still a problem in finding the correct numbers to put into diffusion equation.

Despite the difficulties of finding appropriate diffusivity parameters the analytical models have been used extensively to locate and design stacks for industrial plants. They have been routinely used by the Alberta Energy Resources





Conservation Board and prior to that by the Department of Health to determine the average distribution of pollutants around gas plants. Their popularity stems from the fact that these models are inexpensive and easy to use. At the same time they provide reasonable answers for cases involving flat topography and simple meteorological conditions.

A number of field tests of analytical models<sup>(8) (9)</sup> are reported in the literature. Generally, the resolution of the models appears to be a kilometer or more in space and from two hours to a month in time. Perhaps the most extensive tests of Gaussian Plume models have been conducted by Miller and Holzworth<sup>(10)</sup> in three different cities. These authors were able to report 90 percent of two hour averages correctly within .01 ppm.

Considering the coarseness of the input data, the model results are acceptable. Nevertheless, they are severely limited by their inability to account for the time variation of source strengths, and their limitation to single sources and inert contaminants. Their most severe limitation for routine use for gas plants lies in their inability to account for uneven terrain and unusual meteorological conditions such as fumigation.

#### C. NUMERICAL MODELS

The limitations of the analytical solutions of the diffusivity equation lead to the development of more ambitious models which solve some form of the diffusivity equation numerically, usually employing computers.



The approach generally has been first to numerically solve the equations expressing conservation of momentum of the wind field to account for its modification due to topographical effects or large urban buildings. The velocity distribution thus obtained at each grid point is used in the numerical solution of the convection-diffusion equation (1). The diffusion coefficients for a given geographical area for the numerical models are normally obtained by history matching the existing concentrations. Several recent publications have described methods which can include topographical effect (11)(12)(13) or large urban buildings (14)(15).

Lantz<sup>(13)</sup> et. al. use a modified form of the three-dimensional equation for velocity potential. The modification includes 1) inviscid potential flow at high elevation, and 2) height dependent coefficients which account for surface friction in the boundary layer. This empirical modification causes the horizontal velocities to vary with height. This form of the convection-diffusion equation also includes the terms defining first order chemical reaction (with no interaction of components) and an approximate ground adsorption term. Calculated results from the numerical models are in good agreement with Gaussian Plume models for simple level terrain cases, but for complicated terrain cases numerical model results are different and appear to be more accurate than the plume models.

The state of the art of numerical modelling does not permit yet the theoretical calculation of diffusion constants, however, it does provide for the standardization of the model for a given geographical area and meteorological event by history matching the observed ground level concentrations. The diffusion constants determined in this



fashion can then be used confidently to extrapolate the results to account for additional sources and background concentrations, different wind velocities, or change in plant operations. In addition, these models allow the diffusivities and the wind velocity to become arbitrary functions of space and time. This means that certain meteorological phenomena like the mountain and valley winds, or the land and lake breeze can be adequately accounted for. Numerical modelling allows for transient concentration calculations which enables one to compute concentrations during fumigations and well flaring.

An important advantage of numerical models is that they allow the consideration of the effect of topography on modifying wind field. The problem is illustrated in Figure V-2. The length of the arrows in this figure represents the magnitude of the wind velocity. In the plume models it is assumed that the hill acts as a "sieve" and thus the wind field remains unaltered. With the numerical model, the highest pollutant concentration over a hill may be as much as an order of magnitude<sup>(13)</sup> lower than the plume model due to recognition of the change in the vertical wind direction.

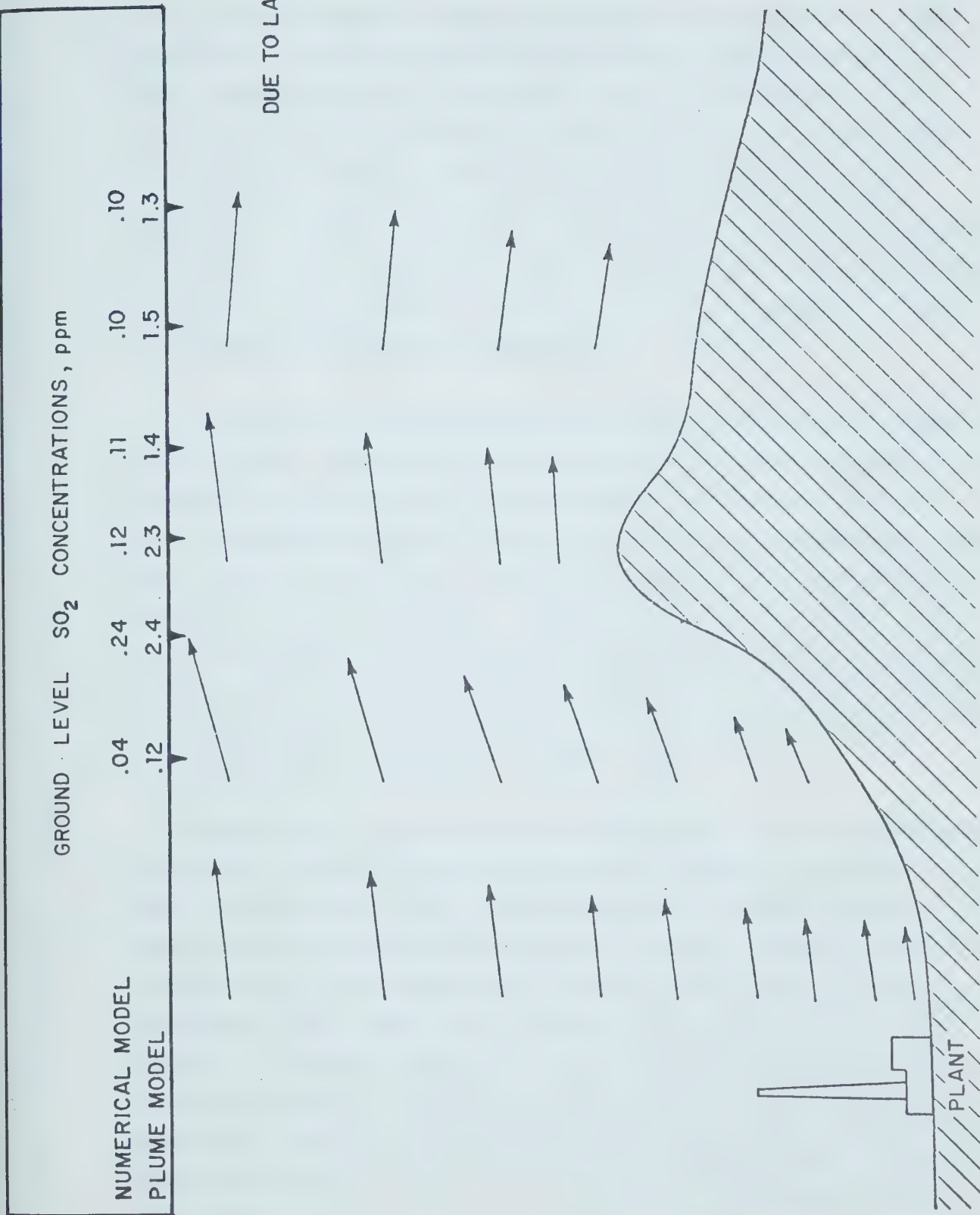
#### D. VARIABILITY OF PLUME RISE ESTIMATES

Under most predictive modelling situations, the value of effective stack height is an influential parameter for ultimate stack design. Effective stack height is the effective emission level of the plume relative to the ground having regard to thermal and momentum rise of the stack effluent as well as the actual stack height.

The rise of a plume of waste gas from a stack depends







CROSS SECTION OF WIND VELOCITIES FOR NEUTRAL STABILITY





upon a considerable number of factors that include stack parameters and variable meteorological conditions. The most important stack parameters are the momentum and buoyancy (or heat emissions rate) of the waste stack gas while meteorological variables include wind speed, air temperature or density and conditions of atmospheric stability. Plume rises for a given set of stack operating parameters also will vary over a wide range under different degrees of atmospheric stability such as unstable, neutral and stable or inversion conditions.

Atmospheric conditions that produce changes in turbulence would affect the rates of dissipation of momentum and heat content of a plume and the resultant height to which it will rise. During period of strong directional wind shear, much lower plume rises would occur as a result of more effective mixing in the atmosphere, reduction in buoyancy and increase in surface area of the plume. Topographical features of the terrain, such as variations in elevation of the surrounding area and heights of buildings at the plant site, also exert a considerable influence on plume rise.

Many plume rise models and formulae have been proposed by various authors to calculate the rise of gas plume for small, medium and large process units or power plants. The analysis of sulphur plant plumes, wherein thermal parameters in particular and momentum parameters are significantly different from these power plant data, is presently under review. A recent analysis of the data on observed versus calculated plume rises from power stacks by seventeen different formulae has been made by Moses and Kraimer<sup>(16)</sup>. This investigation was based on 615 measurements arising from ten different plume rise research programmes using 26 different stacks. For the 615 cases, the mean ratios



of observed to calculated plume rise values from the 17 formulae varied from a low of 0.27 (overestimation of calculated values) to a high of 7.8 (under-estimated).

A summary of the comparative data obtained in the study of Moses and Kraimer is presented in Table V-1.

TABLE V-1

Mean Ratios of Observed to Calculated  
Plume Rise Values  
Moses & Kraimer

Stack Height Range	no. of Obser- vations	Concawe (17)	Lucas, Moore & Spurr (18)	Moses & Carson (19)	Briggs (20)	Holland (21)
Small Stacks	166	1.50	0.16	2.10	0.92	5.33
Intermediate	352	0.69	0.28	1.06	0.84	2.37
Large Stacks (range, about 100-183 m)	58	0.78	0.54	1.11	0.74	0.95
All sizes	615	0.90	0.27	1.33	0.84	3.00

The procedure presently recommended by the Department of Environment<sup>(1)</sup> (Dept. Health) has as its basis the Bosanquet, et.al. procedure. The Department's procedure includes two important modifications. First, an essentially neutral temperature stability condition is assumed to exist; and second, a factor of 75 per cent to the total calculated rise is applied. For a flare stack, a 50 per cent factor is used.

A comparison by Agrawal<sup>(22)</sup> of stable temperature gradient



plume rise calculations made for an Alberta sulphur plant is shown by Table V-2 and indicates the variance possible using "accepted" methods.

TABLE V-2

Comparison of Plume Rise Calculations

<u>Method</u>	<u>Momentum ft.</u>	<u>Thermal ft.</u>	<u>Total ft.</u>
Bosanquet, et. al. (23)	70	400	470
Alberta Dept. Health (1)	50	420	470
Holland	50	180	230
Bosanquet (24)	60	310	370
Briggs (25)	--	300	300
Concawe	--	450	450

From a numerical model history match of measured ground level SO<sub>2</sub> concentrations, the best agreements were obtained using the Holland and Briggs methods; the Holland for wind speeds larger than 5 mph and the Briggs for wind speeds below this value. An interesting fact of this observation is that each method utilizes a different dependence on variables like volume throughput and wind velocity. The Holland formula indicates a direct proportionality of plume rise with volume throughput and an inverse proportionality with wind speed. In contrast the Briggs' expression shows a 1/3 power dependence on volume throughput and between a negative 1/3 and negative 1 power dependence on velocity (the variation depending on atmospheric stability). Thus sensitivity to volume throughput and wind velocity can be quite different when using either of the two different expressions of plume rise.





It is clear that considerable caution must be exercised in the use of a particular plume rise formula for stack design purposes. The subject still requires considerable research to develop a satisfactory plume rise model that will include all of the important factors particularly related to sulphur plant emissions. In the interim, industry generally accepts the Bosanquet et. al. modified calculation when used in conjunction with the Sutton or Pasquill formula because experience has shown that the resulting ground level concentration measured will be well within the ambient air standards. Certain situations may arise where dignificant topographical features may require more involved consideration of stack height calculations and industry and government should appreciate and utilize technical advances made in this regard.



## V STACK DESIGN

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## VI MONITORING PRACTISES

### A. Direct Monitoring

1. Process Monitoring
  - a. Daily Plant Balance
  - b. Routine Operating Control
2. Stack Emission Measurement
3. Ambient Air Quality Monitoring
  - a. Exposure Cylinders
  - b. Dustfall Cylinders
  - c. Continuous Monitoring Devices
    - (i) Types
    - (ii) Calibration
    - (iii) Site Selection
    - (iv) Data Transmission
4. Plume Monitoring
5. Data Interpretation and Reporting

### B. Indirect Monitoring

1. Atmospheric Corrosion
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  - a. General
  - b. Photographic Techniques
3. Vegetation Stress
4. Soil Sampling

### C. Summary

### D. References





## MONITORING PRACTICES

The sulphur recovery operations sector of the gas industry in Alberta since its inception in 1951 and particularly over the last five years, has devised a conscientious emissions surveillance program which, in its technical advancement, thoroughness and size, makes it unique in the world. The measurement and monitoring methods developed have assisted the industry in the understanding and upgrading of the sulphur recovery process with a corresponding reduction in emission levels. The increase of the overall recovery of sulphur in Alberta is demonstrated in Figure VI-1 which shows the sulphur recovery expressed as a percent of sulphur content contained in all gas produced (including flared gas) in Alberta.

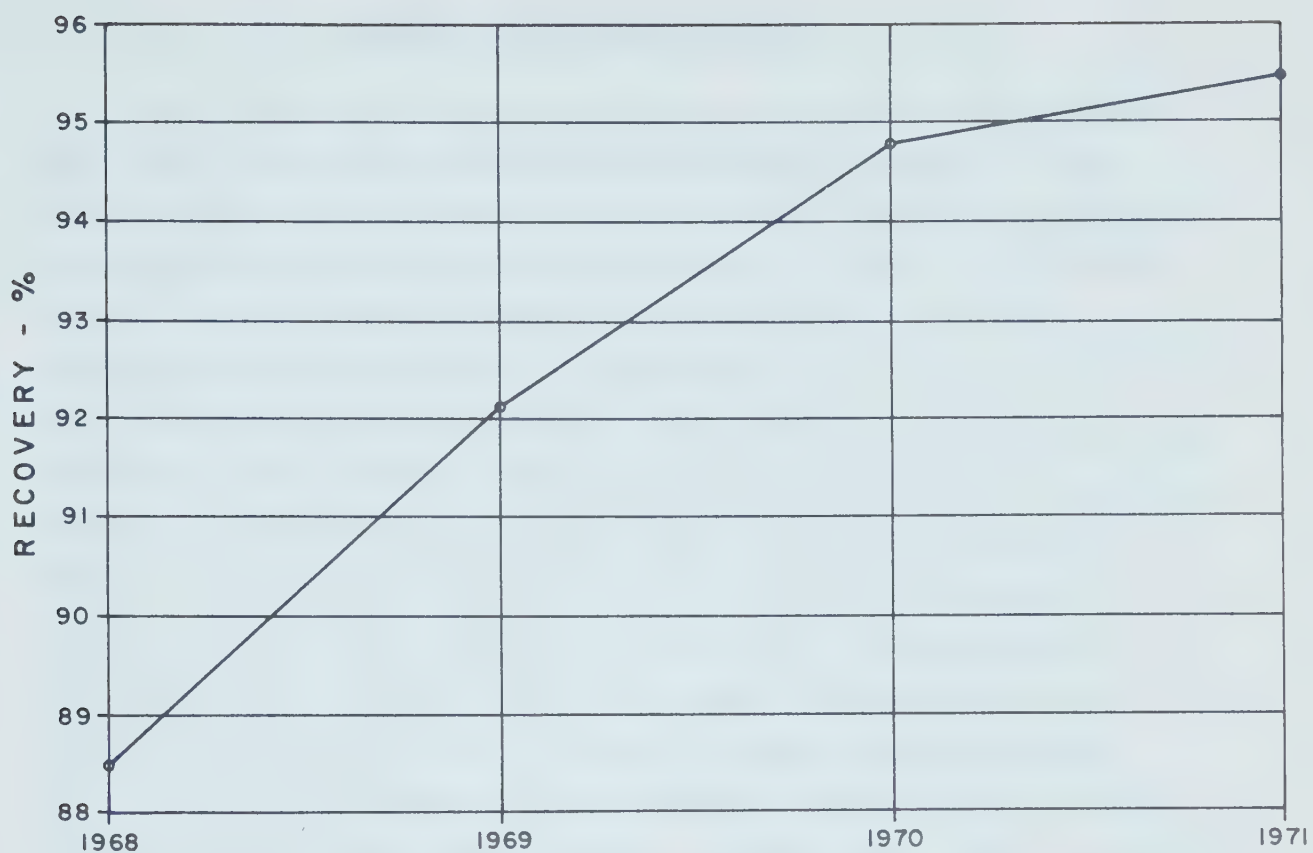
### A. DIRECT MONITORING

#### 1. Process Monitoring

##### a. Daily Plant Balance

Due to diverse ownership of most gas processing plants and the requirements of the Oil and Gas Conservation Regulations, each gas processing plant maintains accurate production records. This involves a daily plant balance showing the gas and liquids received at the plant in comparison to the gas sold and products recovered or flared. With the knowledge of the composition of the gas and liquid streams from routine plant tests, the day's operations are evaluated with respect to recovery efficiency in order to effectively control the operation.





OVERALL INDUSTRY AVERAGE  
SULPHUR RECOVERY IN ALBERTA - %



b. Routine Operating Control

The most recently constructed gas processing plants have sophisticated analyzing and control systems. For those plants where such equipment is not installed, effective control of the processes is achieved by manual techniques. In the latter instance many plants perform wet tests, incorporating variations of the Tutweiler test to determine the hydrogen sulphide content, and a back titration to determine the sulphur dioxide content of gases from various stages of the process system to maintain operating efficiencies. In the larger and more recent plants, operating control samples are analysed using gas chromatography. Process control instrumentation is not a requirement by any regulatory agency. Nevertheless, as early as 1962, process monitoring was applied using gas chromatographs on a continuous basis in the interest of improving sulphur recovery efficiency operations. At the same time, to benefit from monitor data, it became apparent industry required increased knowledge of the Claus reaction and associated factors, such as the condition of the catalyst, changes in feed composition, operating temperatures and the hydrocarbon content of the feed which influence the conversion efficiency.

It is estimated that fifteen plants operating in Alberta now are using some form of process control in their sulphur recovery operations. All of these process control units are believed to be based on tail gas analysis using chromatography. Another approach using the principle of ultra-violet light absorption has been developed recently and is presently under consideration by a number of plants.

One concept in sulphur recovery operations of optimization of the process by closed loop control is indicated in





Figure VI-2. Information on composition and rate of acid gas feed are fed to an analog feed forward computer, while the  $\text{H}_2\text{S}/\text{SO}_2$  tail gas ratio readings are supplied to a feed back computer. These data are weighted to optimize and control the process variables. One such installation has been made in an Alberta plant.

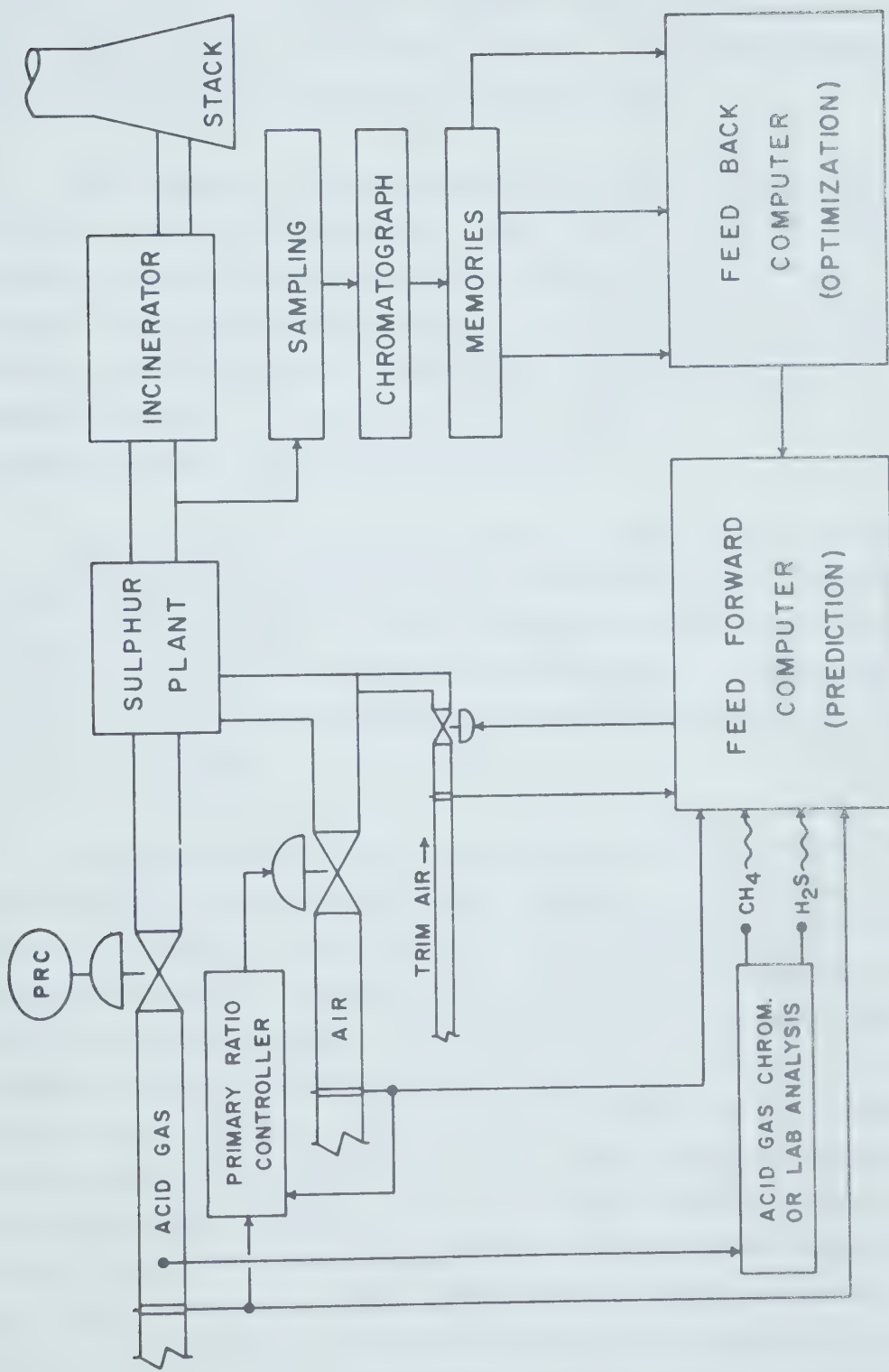
## 2. Stack Emission Measurement

Determination of the emission rate from a stack using conventional methods involves the measurement of the velocity and composition of the effluent gas. The test, which takes about eight hours to perform, is conducted in accordance with methods prescribed by the Department of the Environment. During the survey, every effort is made to hold the operating level of the plant steady at a minimum of 90 percent of the design or approved capacity of the plant.

The effluent velocity is obtained by running a series of traverses across the stack with a pitot tube to which a sensitive draft gauge is attached. Stack temperature is determined by a thermocouple in the gas stream while composition of the effluent is determined by chemical absorption of sulphur dioxide, carbon dioxide and oxygen from a sample of gas drawn from the effluent stream. After each test, a report is prepared showing the effluent velocity, composition, tons of  $\text{SO}_2$  emitted and the plant efficiency calculations. This is compared to the plant material balance data and its calculated efficiency.

In 1970 the ERC Board required some form of continuous monitoring device to be in operation for all plants recovering more than 100 long tons per day of sulphur. In response to this requirement, two types of systems have evolved. The first is one which gives a continuous record of the gas





FRENCH PROCESS OPTIMIZER FOR SULPHUR RECOVERY PLANTS  
USING GAS CHROMATOGRAPHY AND ANALOG COMPUTERS



velocity and concentration of sulphur dioxide from which the sulphur emission rate is computed manually. The second provides a direct record of the quantity of  $\text{SO}_2$  being emitted on a continuous basis. A block diagram of the latter type is shown by Figure VI-3.

Two methods are available for determining the composition of  $\text{SO}_2$  in the stack. The first is by gas chromatography and the second utilizes ultra-violet light. The former has a sampling cycle of one analysis in anywhere from 8 to 12 minutes, depending upon the design of the chromatograph. The ultra-violet method provides an instantaneous, continuous analysis.

As indicated in Figure VI-3, the signals from the primary measuring elements are received by an analog computer from which a direct record of the long tons of sulphur or sulphur dioxide are displayed. The plant operators use this record to observe the emission from their operations.

Difficulties have been encountered in obtaining continuous operation of these devices. The major problems occur at plants with the older type corbel construction concrete stack or those which subsequently had been relined with stainless steel. The distance between the inner and outer sections of the latter stacks are in some instances as much as 10 feet. This makes it difficult to maintain high enough temperatures in the sample stream because of excessive heat losses from the sample lines. Also, in some stacks, refractory material, salts of various types or other materials from side streams admitted to the incinerator for efficient disposal, and other foreign material, lead to plugging of the sample probe and the velocity measuring device. These problems are gradually being over-



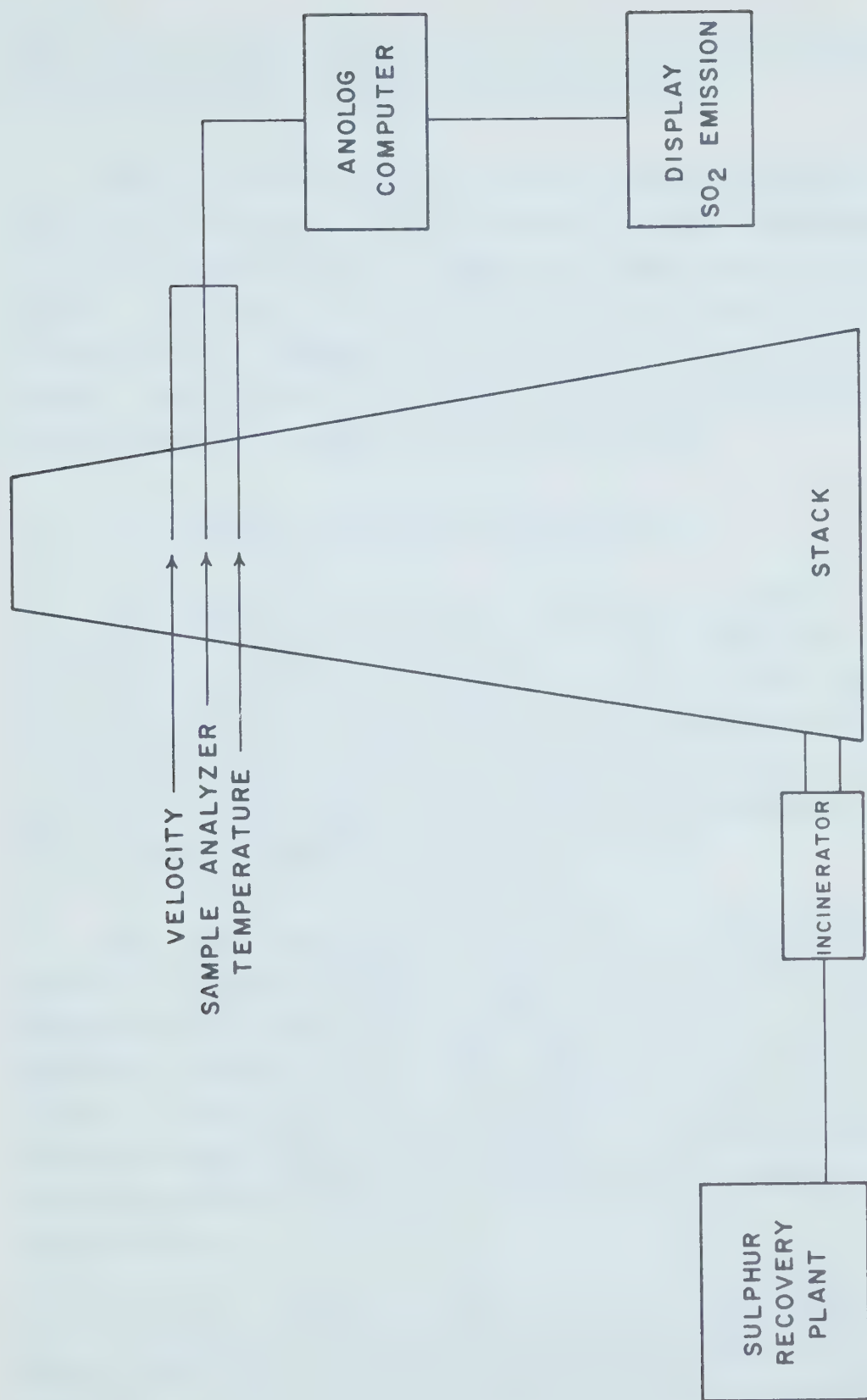


DIAGRAM OF CONTINUOUS MASS FLOW EMISSION MONITOR





come and on stream performance with reasonable accuracy is being obtained 90 percent of the time.

There are 40 sulphur recovery plants operating in the Province of Alberta, of which some 25 have a requirement for the installation of a continuous stack monitoring device. Of these, 15 have mass emission measurement based on ultra-violet analytical methods, and 7 use gas chromatography. Only three use concentration and velocity information to manually compute the emission rate.

### 3. Ambient Air Quality Monitoring

The ocean of atmosphere covering the earth is the repository of an enormous amount of waste material. Air has many self-cleansing processes which, if not overburdened permit the maintenance of a reasonable level of purity in the atmosphere. Waste material has natural (ash from forest fires, volcanoes, dust storms), as well as man-made (industrial effluents) origins.

The most important atmospheric process for handling wastes is simple dilution. There are  $4.9 \times 10^9$  million cubic miles of "useful" air which could safely contain enormous quantities of foreign material if it was adequately dilute. When pollutants are discharged into the air, their dilution and diffusion are related to the prevailing meteorological conditions, which directly influence ambient air quality.

Ambient air quality monitoring by the sulphur recovery plant operators in Alberta goes back to 1958 when the first exposure cylinder stations were installed at a plant in southern Alberta. In 1960, the first continuous monitoring instruments were installed at sulphur plants. Parallel to the monitoring done by industry, the Department of Health



(presently Department of the Environment) maintained surveillance of the air quality around gas plants.

#### A. EXPOSURE CYLINDERS

Exposure cylinder stations are widely used as a practical method of measuring total sulphation and hydrogen sulphide concentrations in ambient air. The exposure cylinder method gives a cumulative, rather than instantaneous, measure of air quality. It is a method intended to determine the relative sulphation from place to place and to indicate long-term trends in pollution level. The method is used to determine any pollution pattern over an area, and to detect trends in the values of sulphation and hydrogen sulphide.

A station is made up of two cylinders, one based on the lead peroxide method for total sulphation, and the other for hydrogen sulphide, using zinc acetate. The lead peroxide cylinder consists of a  $100\text{ cm}^2$  strip of sulphur free gauze fitted around a non-reactive cylindrical holder and coated uniformly with a lead peroxide ( $\text{PbO}_2$ ) paste. When exposed to the atmosphere, the lead peroxide reacts with atmospheric sulphur compounds to form lead sulphate ( $\text{PbSO}_4$ ). The sulphate is measured gravimetrically and reported as milligrams of  $\text{SO}_3$  per  $100\text{ cm}^2$  per day.

For detection of hydrogen sulphide, a similar cylinder is wrapped with a  $100\text{ cm}^2$  strip of filter paper impregnated with zinc acetate ( $\text{Zn}[\text{C}_2\text{H}_3\text{O}_2]_2$ ). Atmospheric hydrogen sulphide reacts with the zinc acetate to form zinc sulphide ( $\text{ZnS}$ ). The sulphide is measured volumetrically and reported in the same units as total sulphation ( $\text{MgSO}_3$  per  $100\text{ cm}^2$  per day).



For protection from mechanical injury and precipitation, both cylinders are sheltered in a small box with metal top and louvered sides.

The use of exposure cylinders goes back as far as 1932 to the Department of Scientific and Industrial Research in England. Since the original applications, subsequent research has been carried out to determine the effect of meteorological parameters on reaction rate and to eliminate sources of error in the preparation and analysis of the cylinders.<sup>(1)</sup>

Studies conducted on the accuracy of the lead peroxide method have indicated the following:

- a. The formation of  $\text{PbSO}_4$  is proportional to the concentration of  $\text{SO}_2$  for the ranges encountered in the atmosphere;
- b. The rate of reactivity is not significantly altered by wind speed or changes in relative humidity, but is affected by changes in ambient temperature or moistening of the lead peroxide surface. The reaction rate was also found to be a function of the  $\text{PbO}_2$  particle size.
- c. Total error of sampling and analysis is estimated to be in the order of 10 percent.

In standard use, care is taken in the preparation of  $\text{PbO}_2$  paste to ensure a uniform and standard particle size. Moisture effects are virtually eliminated by proper use of the louvered shelter.

Further studies have indicated reasonable correlation between total sulphation and  $\text{SO}_2$  concentrations (2, 3). One





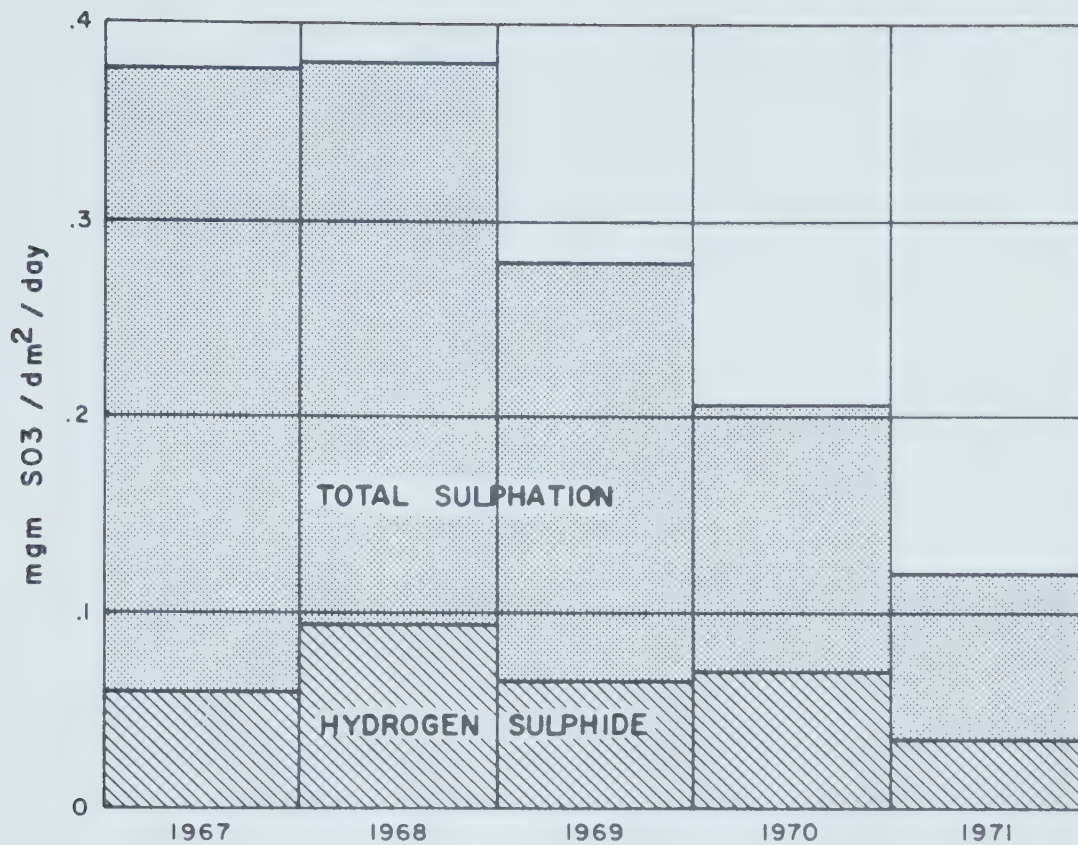
such study was carried out over an eighteen month period in the vicinity of one of Alberta's major sulphur plants (4). Good correlation was found to exist both between the exposure cylinders and wet chemical determination by the modified West Gaeke procedure. No variation in the rate of reaction of the lead dioxide was apparent from summer to winter. In fact, the exposure cylinder results closely followed the trend to higher sulphation values in the winter as indicated by the other two methods.

Great care is taken in the placement of the exposure cylinder stations. Locations of particular interest in the plant vicinity include hilltops, valleys, towns, farm houses, and recreational areas. Other stations are then located to cover the area on a predetermined grid system, with special attention paid to the prevailing downwind direction.

Exposure cylinders were in service in the vicinity of Alberta sulphur extraction plants at over 350 permanent sites in 1971. Plants utilize between 4 and 40 stations, depending on size. The cylinders are changed and analyzed at the end of each calendar month in accordance with standard practices set out by the Department of the Environment, and results are reported to the Department.

The network of exposure cylinders has faithfully recorded the air quality trends in the vicinity of Alberta sulphur plants for the past fifteen years. Distinct correlations have been noted between exposure cylinder data and sulphur recovery efficiency as plants have been improved. A good illustration of this is the record by one of the major sulphur plants in the Province, shown on Figure VI-4.

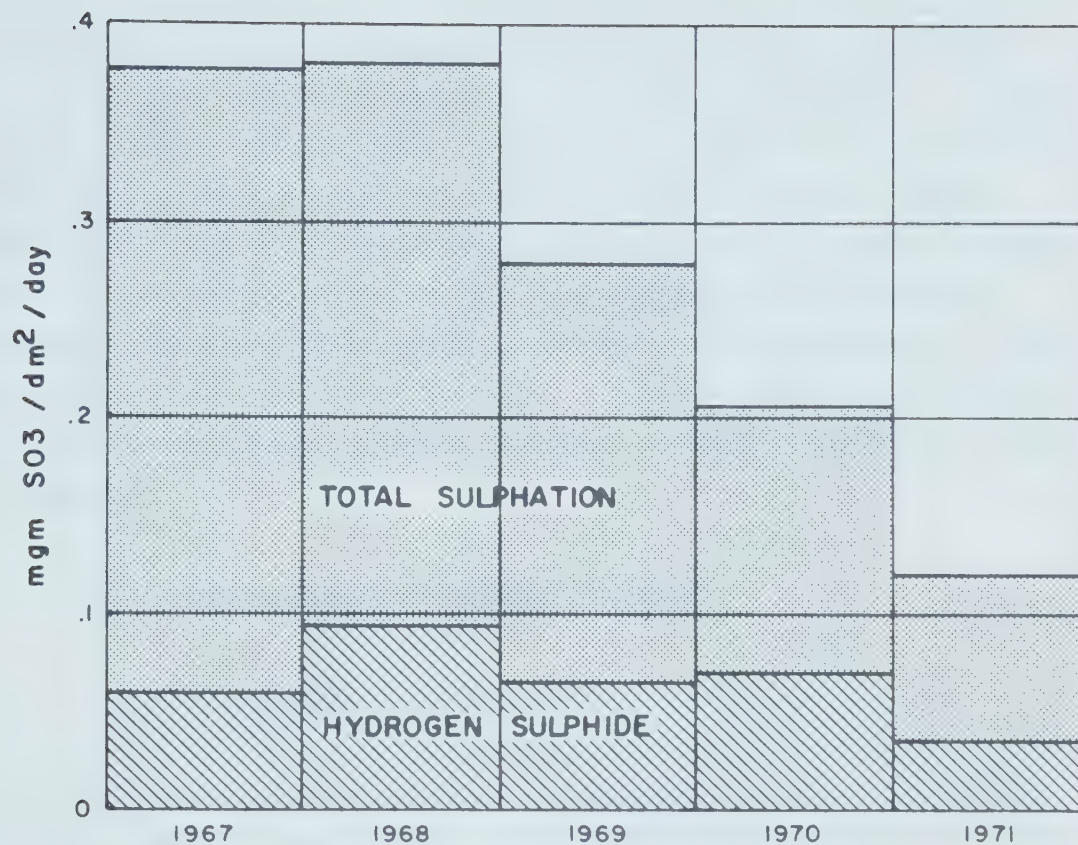




MAJOR SULPHUR RECOVERY PLANT IN ALBERTA

YEARLY AVERAGE TOTAL SULPHATION AND  
HYDROGEN SULPHIDE CONCENTRATIONS FROM  
EXPOSURE CYLINDERS





## MAJOR SULPHUR RECOVERY PLANT IN ALBERTA

YEARLY AVERAGE TOTAL SULPHATION AND  
HYDROGEN SULPHIDE CONCENTRATIONS FROM  
EXPOSURE CYLINDERS





## b. Dustfall Cylinders

The Department of the Environment has recently requested that sulphur plant operators maintain exposure cylinders for the measurement of sulphur dustfall. These consist simply of an open container, mounted 4 to 6 feet above the ground in the vicinity of the sulphur block. These are removed for analysis at the end of each calendar month in conjunction with the sulphation and hydrogen sulphide exposure cylinders. Results are reported as Tons Sulphur per sq. mi. per 30 days. There are approximately 300 such stations presently around sulphur recovery plants in Alberta.

## c. Continuous Monitoring Devices

### (i) Types

Sulphur dioxide in concentrations of physiological concern, may be measured in the atmosphere by one of four analytical techniques; conductivity, colorimetry, coulometry or flame photometry.<sup>(5)</sup> A number of commercial instruments embodying these principles are available. In the conductivity method<sup>(6)</sup>, the electrical conductivity of a solution measured between two immersed electrodes is proportional to the SO<sub>2</sub> content of the air sample drawn through the solution. The colorimetric method uses a chemical test known as the West Gaeke procedure, which is based on the modified Schiff reaction. Coulometric analysis of SO<sub>2</sub> depends upon the redox potential established to titrate sulphur compounds as they are formed in solution. Flame photometry analysis of SO<sub>2</sub> utilizes the specific sulphur luminescence wavelength of 394 per mu provided by a hydrogen rich flame.





Much work has been done and is continuing to be done on the evaluation of sulphur dioxide field monitoring instrumentation for reliability and accuracy (7, 8, 9 and 10). Equipment designs have advanced to increase long term chemical and electronic stability of field instruments to maintain their sensitivity, and to reduce reaction interference problems. Solid state electronic circuitry, improvement in electrical switching mechanisms and greater pump reliability have all contributed to extending the unattended monitoring capabilities of some of the newer instruments.

Instruments used in the detection of hydrogen sulphide employ a colorimetric technique based on the reaction of lead acetate with ambient hydrogen sulphide. The instruments, generally referred to as "spot tape samplers", operate on a one-hour exposure of a section of lead acetate impregnated paper tape. Reaction with hydrogen sulphide to form lead sulphide causes a discoloration on the tape.

Due to the instability of the lead sulphide stain when exposed to air and sunlight, the tapes are interpreted, either manually within 24 hours after exposure, or automatically. Many of the instruments are now equipped with a built-in spot evaluator which measures the optical density of the discolouration at the end of each hour and transmits the value to be recorded on permanent charts.

In practice, these instruments are housed in a trailer and referred to as an Air Monitoring Station. In Alberta, the stations usually consist of an air conditioned trailer equipped with continuous monitors and recorders for sulphur dioxide, hydrogen sulphide, wind direction and velocity. Power to the trailer is supplied from standard



networks or is generated on site.

(ii) Calibration

To ensure the highest degree of reliability and accuracy, a detailed calibration routine is followed for continuous monitors, employing the most accurate and technically advanced procedures available.

For some years, the established reference method for determining low level concentrations of sulphur dioxide has been the West Gaeke procedure. Recent developments in the permeation of gases such as  $\text{SO}_2$ , through a porous structure, has led to this method becoming a secondary standard to the West Gaeke method.

In the permeation system, the sulphur dioxide exuding from the tubes is mixed with a diluent gas stream, and the resulting mixture supplied to the instrument. The permeation rate of the sulphur dioxide is determined gravimetrically and the total gas stream flow rate is metered by a calibrated flow control device. During each calibration generally four concentrations within the range of the instrument are supplied to the instrument.

In order to assure that the permeation system is operating correctly, the sulphur dioxide concentrations delivered by the permeation tube systems are checked by the modified West Gaeke method. The procedure is carried out a minimum of once each month on all operating instruments in accordance with Department of the Environment Air Monitoring Directives.

Some instruments now in use contain an internal calibration mode, which is checked periodically, while the



instrument is in operation. In the event of a deviation in the internal calibration, the instrument is immediately recalibrated by the permeation tube and West Gaeke procedures.

(iii) Site Selection

Since the purpose of the continuous monitor is to detect the maximum sulphur dioxide and hydrogen sulphide concentrations existing in the vicinity of a plant, care must be taken in positioning the instruments. Generally, a number of factors are involved in the selection of the optimum location for a trailer:

- Average wind direction: The instruments are generally located downwind of the plant in the direction of the most frequent wind.
- Topography: Where possible, the trailer is located on nearby hills or ridges where topographically induced turbulence effects should be noticeable.
- Pollutant Distribution: Accumulated data from the exposure cylinder networks are utilized to determine the location of the maximum sulphation level.
- Receptors: When two or more stations are being located, at least one is located in the general area of built up or cultivated areas, where potential pollutant effects may be most damaging.

Once the general location has been chosen, the specific





site is determined on the basis of accessibility, absence of structures which may interfere with the micrometeorology of the site, and absence of any obvious sources of contamination.

The number of trailers and length of monitoring time depends on the size and location of the plant. The Department of the Environment requires that monitoring be conducted for at least two months of the year at thirty-five sulphur extraction plants in Alberta. Of these, fourteen plants maintain between one and seven stations continuously. In 1971, continuous air quality monitoring at sulphur plants in the Province amounted to approximately 377 trailer-months, representing a cost to industry of about half a million dollars.

#### (iv) Data Transmission

The current trend in Alberta is to transmit or telemeter air quality data from several remote locations to one central control room or operation centre. This procedure permits the continuous image of the air quality to be monitored as indicated by the isolated instruments.

Analog telemetry is accomplished by using one of several techniques: A DC voltage, frequency shift variable keying, frequency pulse with keying, or by digital or binary pulse techniques. Short-haul radio links, rather than telephone lines or dedicated cable, permit easy location changing of monitoring trailers. Line-of-sight between relevant antennae is not necessarily a requirement, but low power and high-gain antennae are mandatory.

#### 4. Plume Monitoring

Because areas of SO<sub>2</sub> stressing may occur at locations



well removed from the point of emission as well as near a plant site the airborne measurement of plume structure and position may be important considerations in any emission analysis. In order to complete the picture of atmospheric transport, a method of measurement is required that will allow the plume concentration profiles to be mapped under various synoptic conditions.

During the last decade a method for remote measurement of some atmospheric gas burdens (called correlation spectroscopy)<sup>(11)</sup> has been pioneered and developed. This technique compares a replica of an adsorption spectra to a dispersed light beam which has passed through the target gas. The quantity of the gas in the light beam is determined by measuring the intensity of the energy in selected wavelengths. The light source for field measurements can be either natural sunlight or an artificial lamp located at a distance from the instrument. Presently available is a portable system that can be mounted in a vehicle for rapid traverses of the plume in any desired location. Such versatility makes it possible to measure total gas burdens or gas concentrations at specific locations.

In order to measure total gas burden the instrument is tuned to respond to the ultra violet component of natural sunlight. The viewing field of the sensor is directed vertically upward through the plume as illustrated in Figure VI-5. In this configuration, the total amount of SO<sub>2</sub> gas in the plume above any particular point is measured. The amount of SO<sub>2</sub> burden above the point can be expressed as a weight per unit area (milligrams per square meter) or as parts per million times the optical path length through the plume (ppm meters).

In order to measure concentration profiles in the



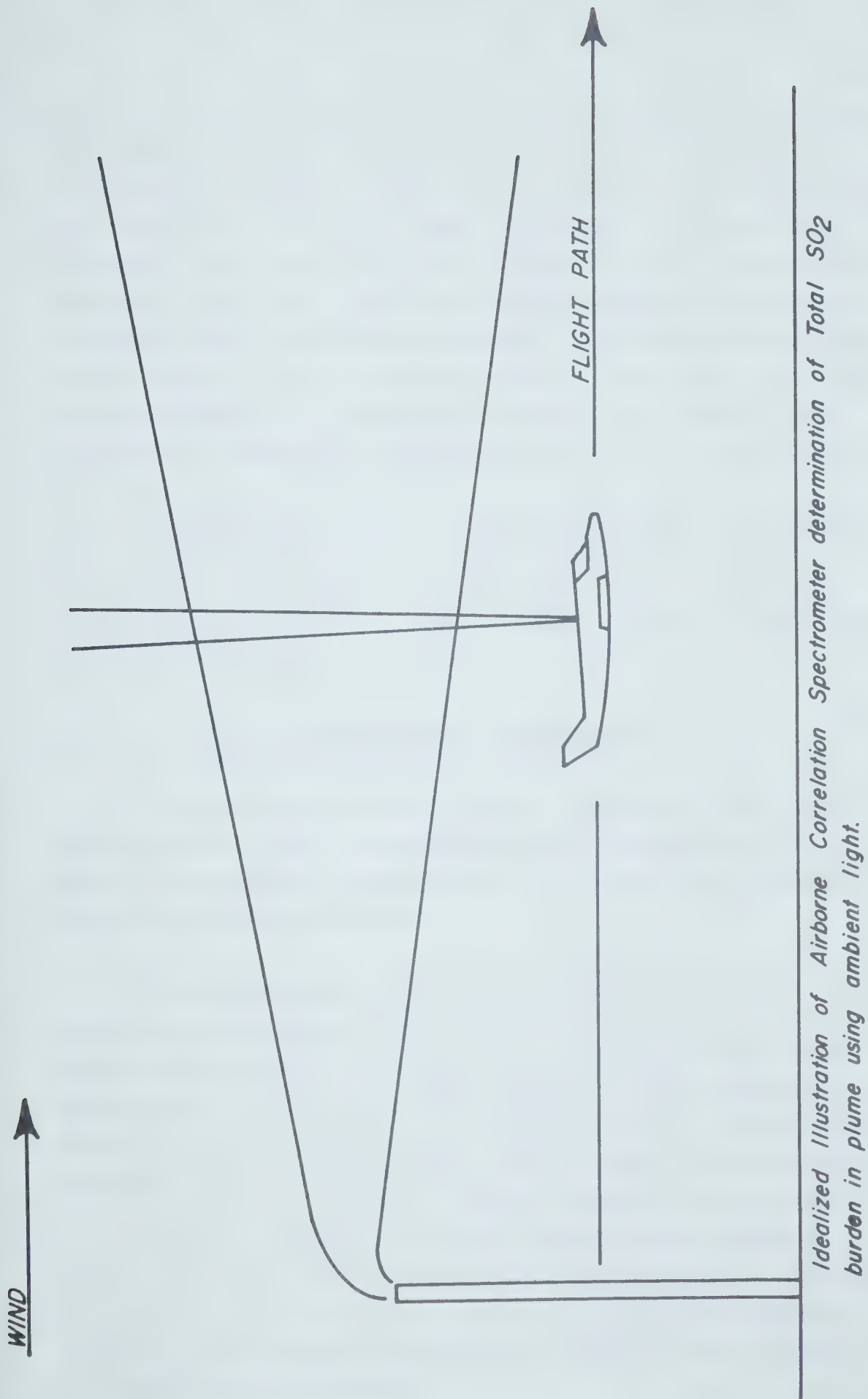


Figure VI-5





plume, the light path over which the instrument senses the gas burden must be reduced and contained. This is accomplished by using an artificial light source (quartz-iodine) and reflecting the light beam around the perimeter of an aircraft with special mirrors attached to the aircraft wing tips and tail cone. The ultraviolet beam then enters the aircraft cabin and the spectrometer from the opposite side of the aircraft to the light source. Since the light beam is restricted to a closed path around the aircraft, the instrument senses the concentration at the aircraft location.

By selecting flight lines of appropriate horizontal and vertical spacing, horizontal and vertical profile sections of the plume can be plotted. The technique is depicted in Figure VI-6 while results of such a survey are depicted in Figure VI-7.

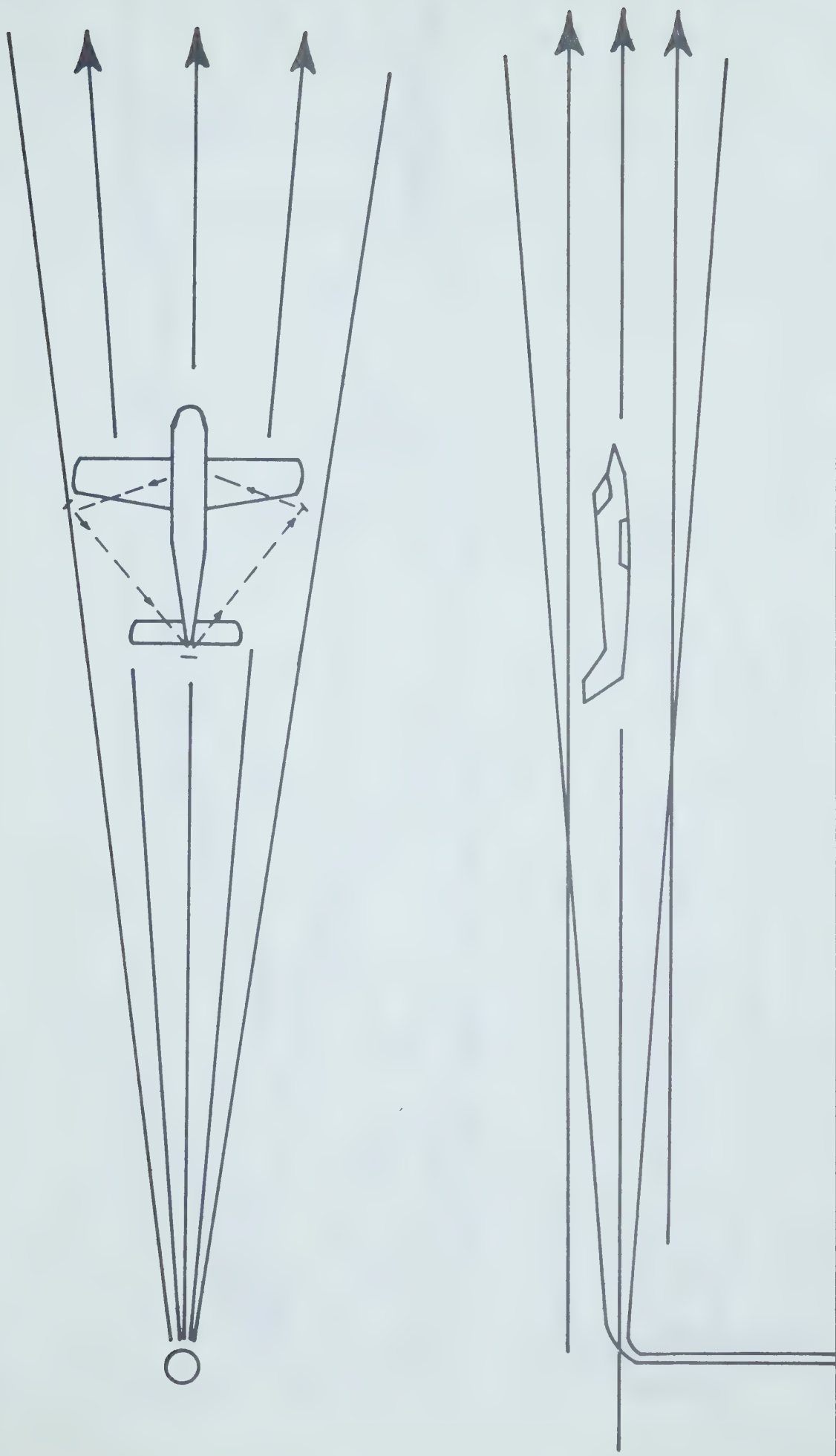
#### 5. Data Interpretation and Reporting

Over the past several years, procedures have been developed for data interpretation and presentation which assure the optimum utilization of collected air monitoring data from surface stations.

The Department of the Environment has recently standardized reporting practices through the issuance of a series of Air Monitoring Directives. In compliance with these, the plant operator each month submits a comprehensive report to both the Department of the Environment and the the Energy Resources Conservation Board. This report includes details of the monitoring network, results from all monitoring instruments, exposure cylinders, and sulphur dustfall stations, and plant operating data for the month. Reference is also made to any report of  $\text{SO}_2$  or  $\text{H}_2\text{S}$  concentrations exceeding the Ambient Air Quality Standard, and a description of remedial action taken.

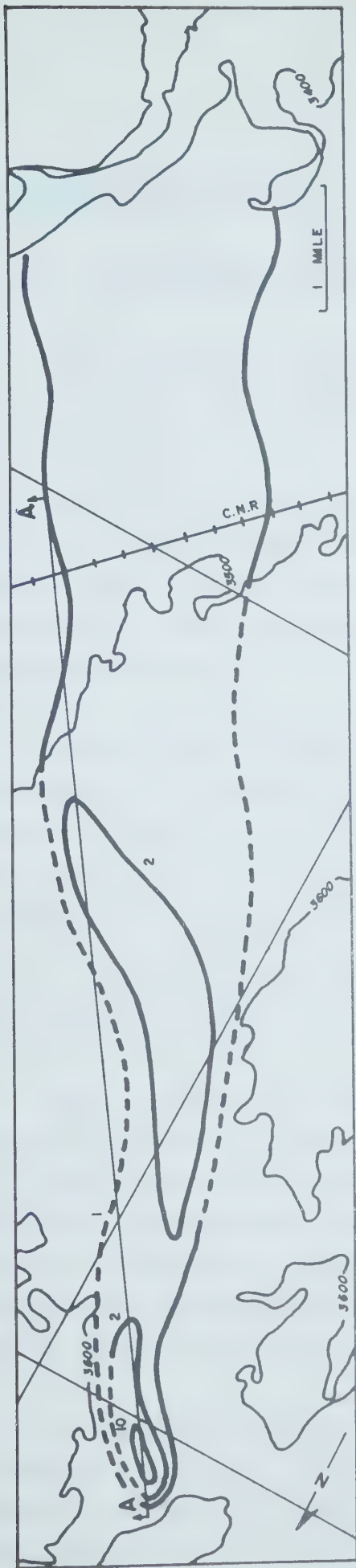




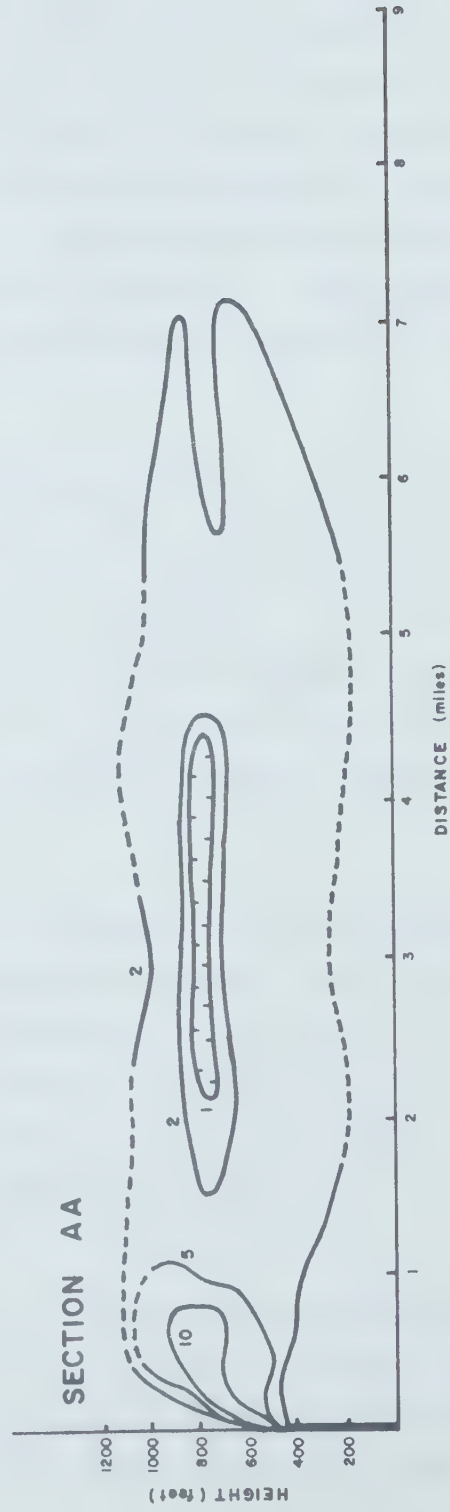


*Idealized Illustration of Airborne Correlation Spectrometer determination of  $\text{SO}_2$  plume profile using closed circuit light system.*





BALZAC PLANT EXHAUST SO<sub>2</sub> PLUME (at 600')



BALZAC PLANT - SOUTH SO<sub>2</sub> PLUME IN PLAN VIEW & PROFILE



## B. INDIRECT MONITORING

### 1. Atmospheric Corrosion

During the last 25 years, some interest has been shown concerning mechanisms of atmospheric corrosion. A number of survey on the corrosion rates of metals have been conducted in the last few years in Europe, the United States and Canada. These have been principally in industrial urban environments where several atmospheric pollutants may interact with possible synergistic effects. A program was instituted in 1957 to monitor atmospheric corrosion rates throughout Alberta.

The corrosion coupons and samples utilized in Alberta were chosen to represent materials that may be subject to corrosive damage in the vicinity of sulphur recovery plants. Such materials as used galvanized telephone wire, two types of common barbed wire, and two mild steel coupons, one of which is zinc coated, are used. In addition, the stations used in Alberta include four samples of common house, barn and implement paints.

The corrosion station is analagous to the exposure cylinder in that it gives cumulative, rather than instantaneous indications of pollution effects. Moisture effects, temperature variations, and climatic conditions can have a marked effect on corrosion rate. For this reason, stations are exposed for at least one year and great care must be taken in interpretation of the results.

In 1971, reference stations were established at eight different locations throughout the province. These were chosen to establish background levels of atmospheric corrosion that may be associated with such factors as urban





pollution, meteorological conditions and agricultural operations. Stations were also established in remote plains areas, where corrosive action is expected to be minimal. As a check on repeatability of the measurements, two stations are maintained at each location. The reference stations are changed and analyzed once a year.

A number of Alberta sulphur plants have now adopted the corrosion station as a monitoring tool exclusive of regulatory requirements. At the present time, at least nine sulphur plants in Alberta maintain sets of Corrosion Stations in their surrounding areas. In 1971, this private network totalled almost 100 individual stations.

The location of the corrosion stations in the field is chosen with the same care and in the same manner as for any monitoring device to provide information that is most meaningful and most easily interpreted. They are set out generally on a pre-determined grid system with locations selected on hilltops, in open areas, near farm houses and in recreational areas. Where an exposure cylinder network is also maintained, the corrosion stations are usually placed in conjunction with the exposure cylinders. This allows correlation of observed atmospheric corrosion with total sulphation.

Based on the reference results to date, the most corrosive atmosphere appears to be associated with agricultural activities. Urban centres indicate slightly lower corrosion rates, similar to remote humid regions. Plains and low brush regions as expected, indicate low corrosion effects. Corrosion rates around isolated sulphur plants were found lower than those in urban situations or in rural areas where air-borne fertilizor dust or acid vapours may occur from agricultural operations.



The use of corrosion stations in Alberta represents a unique development in monitoring of pollution effects in that it is only in Alberta that stations are maintained to monitor the atmospheric corrosive effects resulting from a single isolated industry.

## 2. Remote Sensing

### a. General

Remote sensing is the technology of obtaining information about a target without having the sensor come in contact with it. The human eye is the oldest and one of the most sophisticated remote sensors. A camera similarly obtains data and records it on film; other sensors and sensor systems "look at" targets for study and obtain particular data about them.

All remote sensing instruments accomplish their function by virtue of their being sensitive to electromagnetic energy that is reflected or emitted from the target. The process of reflection is "active" and is the result of the target being illuminated. Part of the illumination energy is directly reflected at or near the target surface. The quantity and quality of the reflection gives target shape, colour, and tone information to the remote sensor. The eye and the camera permit the distinguishing of objects based entirely on the reflections which produce impressions and images of target characteristics. The process of emission from a target occurs whether it is illuminated or not. Emission is a "passive" process and is an innate property of all matter in some frequencies. For example, radio activity is a passive property of some objects and occurs regardless of the illumination present. All objects



that have a temperature above absolute zero emit IR energy randomly into space. The intensity of the emission is proportional to a power of the absolute temperature. To take advantage of this relationship, instruments have been developed that are sensitive to emitted energy which permits the identification and characterization of targets.

It is important to recognize that the sole purpose of remote sensing (a technology involving many techniques) is to make it possible to identify and characterize targets in the environment based on their spectral properties. Since all objects have characteristic spectral signatures, it follows that many targets that are "invisible" or have obscure signatures in one part of the spectrum, may produce pronounced spectral effects in other parts. Hence the need in general environmental research, to employ many remote sensing techniques. For example, if  $\text{SO}_2$  stress in coniferous trees is not identifiable in the visible using colour films, it may be identified according to its thermal signature in another spectrum range.

#### b. Photographic Techniques

Wave lengths in the visible spectrum may be registered with black and white, and colour film. More recently, rather exotic film formulations with unusual colour registrations have become available. One useful film is called "false colour" IR, which has pronounced sensitivity in the yellow, orange, red, and very short images on this film are very unlike true colours, hence the term "false colour".

FCIR film has a strong response to vegetation. Plant cells containing chlorophyll reflect in the red but this colour is normally masked by the presence of an abundance of green energy. The red is therefore seen only if blue-green





filters are employed or if the film formulations are insensitive to blue and green.

The reflectance of red energy by vegetation is a tool that can be employed in the diagnosis of certain vegetal stresses at some plant growth stages. In general, the quality and quantity of red reflected from vegetation is governed by leaf morphology, and physiological condition. Healthy, green, turgid vegetation reflects strongly in the red and photographic IR regions.

The useful interpretation of FCIR photos to obtain vegetation stress is very much a "black-art" and the talent is acquired mainly by long experience. Films and formulations change annually, and exposures and developing chemistry are sensitive and difficult to control. Nevertheless, it is a useful technique in environmentology.

### 3. Vegetation Stress

During many days of the vegetative season, there are periods when vegetation is likely to be under normal environmental stress. Such stresses are caused by the surplus or shortage of soil water, surplus or shortage of heat, surplus or shortage of nutrients, etc. In natural stands, the variation is enormous, particularly in more severe terrain. In such cases, earth-sun geometry causes some hill sides and slopes to become over heated and to have thin or gravelly top soil supporting a limited plant population. Moreover, these natural stresses vary through the day and season. It is therefore very important that aerial photography and FCIR film be used with these considerations in view.





#### 4. Soil Sampling

All effluents discharged into the atmospheric environment are eventually absorbed by various life cycles in nature which soon become involved at the surface of the earth. Indications of the deposition of such materials on the surface may be found in the vegetation and soil. This is particularly true of elemental sulphur dust which, though capable of becoming airborne, settles to the soil surface very near the gas plant. Nyborg and Schurer<sup>(12)</sup> show that "When elemental sulphur is added to soil, certain soil bacteria (of the genus Thiobacillus) oxidize the sulphur to sulphuric acid as follows:



The rate at which sulphur is oxidized varies greatly from soil to soil and depends on such conditions as temperatures, moisture, aeration, fineness of the sulphur deposited, and number of Thiobacillus bacteria present in the soil. The acidification reaction proceeds most rapidly when soils are warm, moist, and well-aerated. Rate of oxidation may be initially limited by number of bacteria, but after sulphur is deposited the bacteria soon build up to their maximum number. Finely-powdered sulphur is oxidized much more rapidly than coarse sulphur. Sulphur finer than 100 mesh may be oxidized about 50 times more quickly than sulphur 5 to 10 mesh in size. Lumps of sulphur (say greater than 1 inch in diameter) are oxidized very slowly until broken down in size.

Most natural soils have pH values in the range of 6.0 to 8.0 which is suitable for good growth of the majority of plant species. Some very sensitive plants, such as alfalfa, do not grow well when pH is below 6.0, but most



species grow fairly well at pH values down to 5.0 to 5.5. In the pH range of 5.0 to 5.5, the aluminum in soils, which is toxic to plants, starts to become soluble. Some plant species are much more tolerant than others to aluminum toxicity (and to other toxicities found in acid soils) and will grow after a fashion in soil as acid as pH4. However, soils of less than pH4 are essentially barren.

Oxidation of 1 or 2 tons of sulphur dust per acre will lower soil pH by about 2 pH units, and oxidation of more than 3 or 4 tons\* will acidify most soils to less than pH4 and will retard or prevent plant growth. The first effect of acidification is a change of species of plants growing on a soil to those most tolerant to acidity. If acidification continues, plant growth will gradually disappear altogether.

Soils are sampled generally from surface to 6" of depth and sometimes in addition, below this depth to qualify the extent of sulphur acidification of the soil. The samples are prepared for testing by drying, grinding and screening. pH and conductivity measurements are made on the water phase resulting from a soil-water mixture shaken for 30 minutes followed by a settling period.

Western soils are usually high in free lime and this reflects the geological origin of the soil and has little effect on crop growth. Normal sulphur or sulphur dioxide conversion to sulphuric acid in the soil or in the atmosphere results in conversion of this lime to  $\text{CaSO}_4$ , an insoluble salt with little adverse effect on crop growth. Chemical reactions with sodium salts in the soil result in a soluble sulphate being available to plants as a fertilizer.

\* It is assumed the author means 3 or 4 tons "per acre".





In nature the soil system has a great capacity to absorb and decompose waste materials. Soil is enormously complex and if its various processes are not overtaxed, it can accomodate many minor "foreign" intrusions.

### C. SUMMARY

The Canadian Petroleum Association believes that the application of emission standards is an inappropriate approach to environmental management, and further submits that "emissions" as such, are not intrinsically related to anything except gas-plant processes. The engineering approach of the last 15 years has lead pollution management and abatement into a situation that satisfies design criteria, but almost totally neglects the most important consideration, vis: it is the receiving environment that is paramount; the environment will determine where the gas-plant and stack should be; the environment will determine what the acceptable emissions level should be, and therefore, what process modifications should be made.

The environment is very resilient, it has the capacity to absorb, even suffer, and then recover if it has not been too seriously imposed on. This natural built-in capability of nature to absorb, makes it necessary to watch natural processes carefully, in order to differentiate between natural and induced environmental changes. This alludes to the pointless program of purely emissions control, to the exclusion of environmental monitoring. Some facets of nature are able to absorb more effluent than others. Regional considerations suggest that gas-plant emission be governed by meteorological and environmental conditions.

It seems to us then, that before increased gas-plant efficiencies are legislated, consideration must be given to the receiving environment. If it can be established





that gas plants, on an individual basis, have caused no environmental degradation, there is no logic to requiring increased sulphur recovery efficiencies.



D. REFERENCES FOR SECTION VI- MONITORING PRACTICES

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VII     SULPHUR RECOVERY, RESEARCH AND DEVELOPMENT

- A.     The Sulphur Plant
  - 1. General
  - 2. Front-End Reaction Furnace
  - 3. Claus Catalytic Converters
    - a. General
    - b. New Catalysts
    - c. Ratio Control
    - d. The Temperature Factor
- B.     Tail Gas Incineration
- C.     Tail Gas Sulphur Recovery
  - 1. Methods
  - 2. Economic Considerations
- D.     References



## VII SULPHUR RECOVERY, RESEARCH AND DEVELOPMENT

### A. THE SULPHUR PLANT

#### 1. General

While it is commonplace to refer to the overall efficiency of sulphur recovery in a sour gas processing plant it is important to recognize that this overall figure is the combination of the efficiencies of a number of component parts in the total hydrogen sulphide to sulphur conversion system. Within the sulphur plant itself there are three clearly differentiated sections - the front-end reaction furnace, the Claus catalytic converter and the tail gas treating section. Each of these sections will be considered separately and the industry's efforts to improve the performance of each one will form the basis for subsequent paragraphs. Figure 1, however, is of importance at this stage as it illustrates the interdependence of these various stages and the manner in which the efficiency of operation of an upstream unit determines the load on a downstream component. This is of particular importance when considering tail gas desulphurization methods and costs.

Figure VII-1 also illustrates one of the biggest problems in achieving high conversion efficiencies - the concentration problem. As we progress through the system the residual unrecovered sulphur values become progressively diluted by other reaction products and added inerts, and are thus harder to remove. By far the largest proportion of the hydrogen sulphide removed from the sour gas is converted to





# THE CONCENTRATION PROBLEM

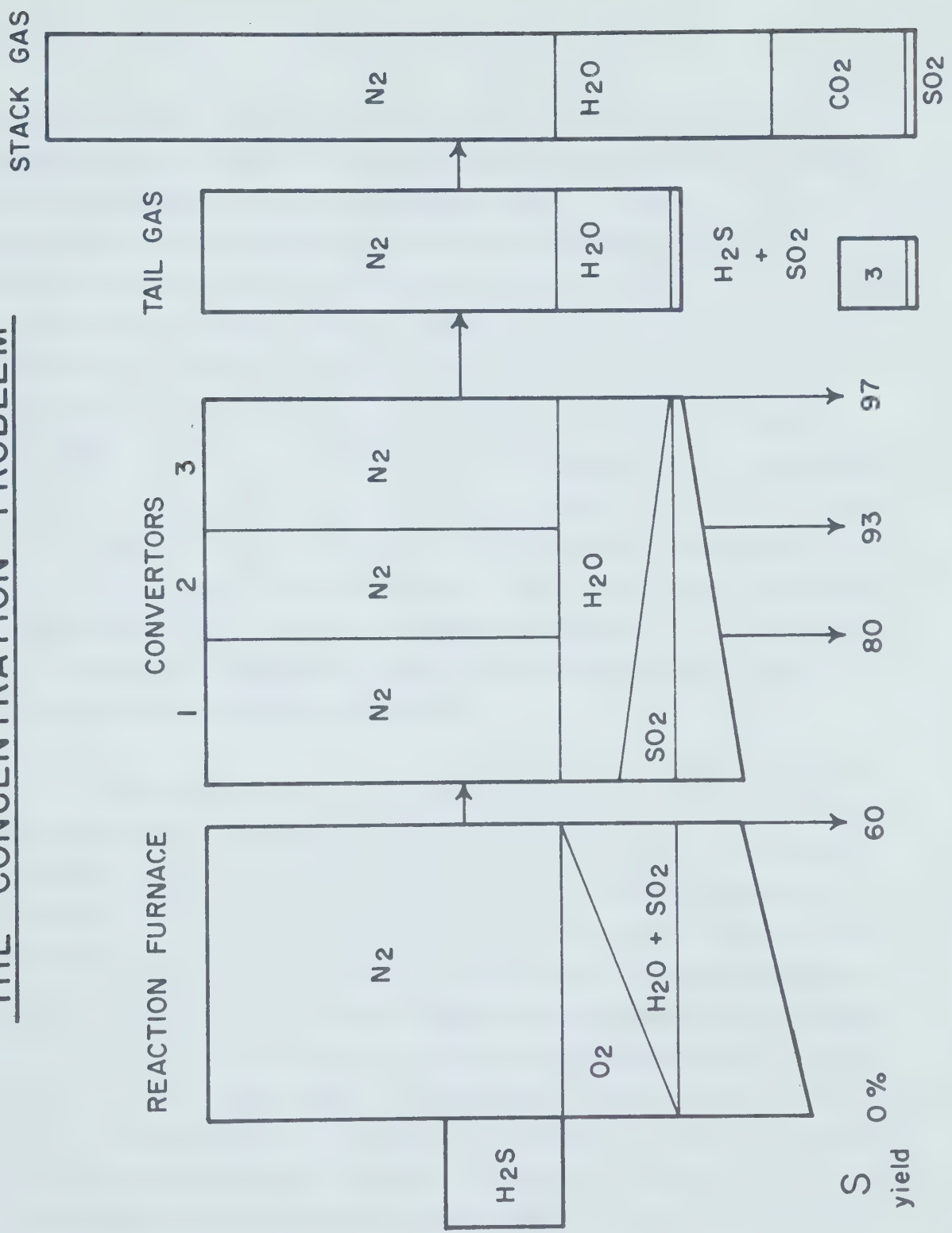


Figure VII -



sulphur in the front-end reaction furnace. Figure VII-1 indicates an average 60% conversion although this depends on many factors to be discussed later. Here, in the reaction furnace, air is added to sustain combustion and the first major dilution of the sulphur content occurs; the nitrogen of the air is inert and is simply "a passenger" from this point on. Enriched oxygen feeds have been investigated and the TRW S-100 process, using liquid oxygen with no nitrogen diluent, is presently being developed. It is, however, not adaptable to current sulphur plant operations and is sensitive to liquid oxygen pricing in such a manner as to make it impractical for large scale Alberta sulphur plant operations at this time. Such very high temperature processes using what in essence is "space age" technology may, however, represent a next generation replacement for the front-end reaction furnace.

The conversion load placed on the Claus catalytic stages clearly depends on the efficiency of the front-end reaction furnace. Since each of these catalytic stages converts the feed received from the previous stage to an equilibrium point the sulphur yield at each stage is determined in part by the efficiency of the previous stage. Industry has done much to improve the overall efficiency of the Claus converter section of the system, both by increasing the efficiency of operation of the individual stages and by increasing the number of stages. Single stage Claus trains are virtually unknown in larger Alberta plants, while three stage converters are now common and even four units in series are available.

The sulphur content of the tail gas stream is obviously determined by the efficiency of operation of the upstream units. The figures of sulphur yield used for purposes of illustration in Figure VII-1 indicate a 3% sulphur content



in the tail gas. Under the new ERCB guidelines incineration of this level of sulphur containing tail gas and venting to the atmosphere would not be acceptable for plants with over 1000 tons per day sulphur throughput. Since 97% overall conversion in a three stage Claus plant is a high conversion efficiency and close to optimum with present plant design, the possibility of tail gas desulphurization before incineration and atmospheric venting has now become an important consideration. This third phase of sulphur plant operation will receive detailed attention in a subsequent paragraph.

Stack gas dispersal, meteorological and topographic factors that influence the ability of the environment air volume to accept and dilute effluent, natural conversion of gaseous pollutants to non-toxic end products and many other factors external to the plant are all aspects of the problem of handling the residue from an otherwise highly efficient industrial chemical conversion system. The gas processing industry has not been satisfied with the "dilution solution to pollution". It has worked continually to improve the efficiency of each component of the sour gas processing system thus minimizing environmental contamination not simply by effective dispersal techniques, but by reducing the total waste effluent from its plant operations. How these improvements in plant operating efficiency have been accomplished and how the industry continues to tackle the ever harder problem of moving closer to the elusive goal of 100%-perfection-is the subject matter of the following sections.



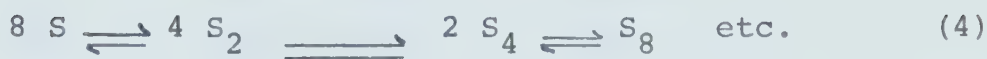
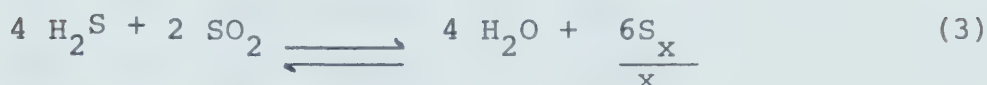
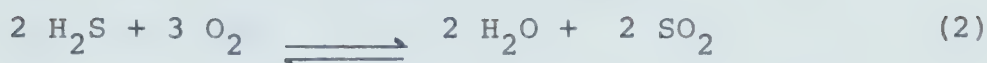
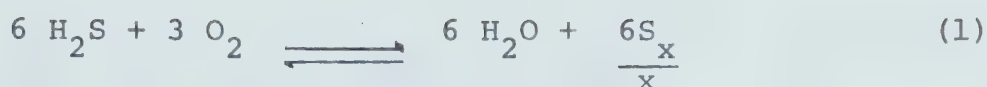


## 2. Front-End Reaction Furnace

The overall efficiency of a sour gas processing plant is determined by the performance of its several component parts. Current emphasis on environmental quality control has focused interest on improvements in downstream units of the plant process stream. Particular attention has been paid to the Claus catalytic section and to tail gas clean-up processes. These downstream components, however, do no more than handle that part of the sour gas feed stream that is not converted to product sulphur in the front-end reaction furnace. What is sometimes forgotten is that under normal circumstances more than 50% of the conversion of hydrogen sulphide to elemental sulphur takes place in the front-end reaction furnace. What is being done to optimize the conversion efficiency in this first section of the typical sulphur plant?

Over the past several years, attention has been directed to achieving better percentage conversions in the front-end reaction furnace. This has led to a wider recognition of the complexity of the chemical processes occurring in the reaction furnace and, in turn, to a re-examination of some design factors not previously considered to be of crucial importance. By and large, design criteria have been based on the assumption that the overall stoichiometry shown in equation (1) serves to describe the process adequately, and refinement, where necessary, need not go further than dividing this process into two steps shown in equations (2) and (3) with additional consideration being given to the equilibria between various forms of the product sulphur indicated in equation (4).



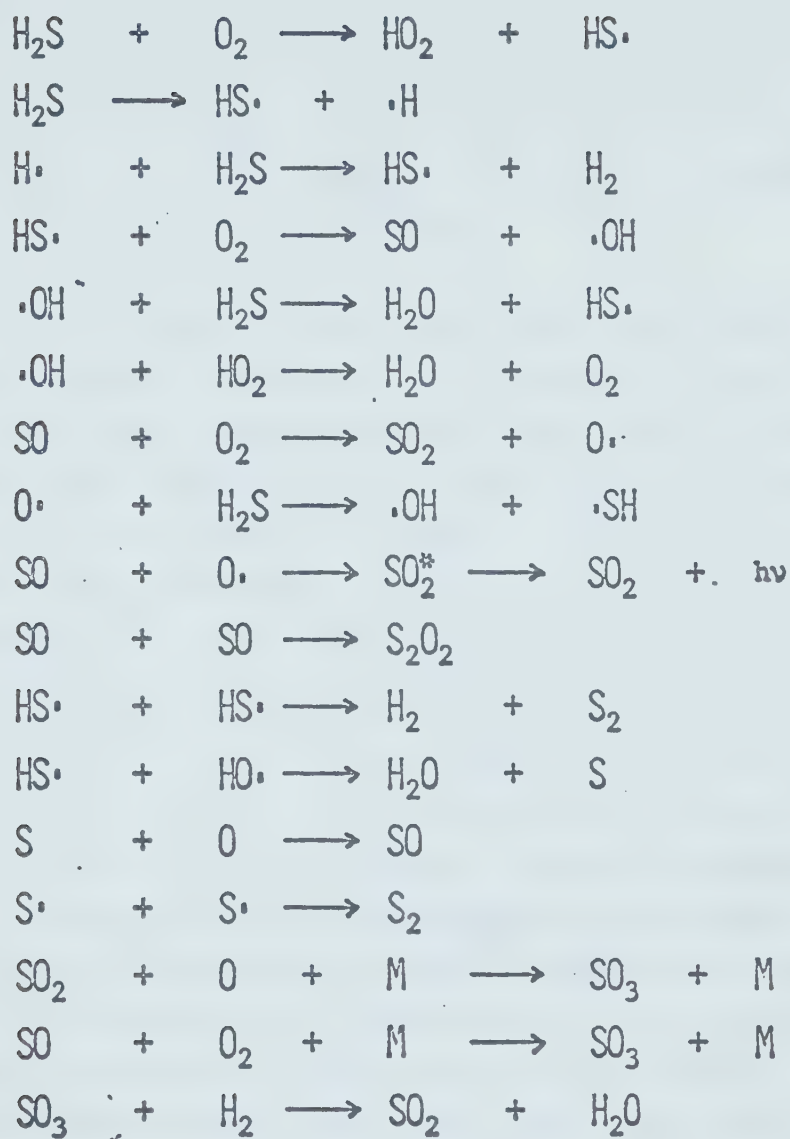


Even a cursory examination of equations (1) to (4) makes it clear that they do not tell the whole story. It is well known, for example, that sour gas process streams typically contain measureable concentrations of molecular hydrogen downstream of the front-end reaction furnace. Indeed, this hydrogen can be used to advantage in some tail gas clean-up processes. None of the equations shown above give any indication where this hydrogen is produced in the furnace processes. Sulphation of the catalyst beds has long been a problem in some gas processing plants and is known to be due to the production of sulphur trioxide upstream of the catalyst section. Again equations (1) through (4) give no indication of where this sulphur trioxide might originate.

Largely as a result of the detailed hydrogen sulphide flame studies of Merryman <sup>(1)</sup> and the extensive work on the combustion of gaseous sulphur compounds recently reviewed in excellent detail by Cullis and Muleaky <sup>(2)</sup>, It is now well established that the true picture of the hydrogen sulphide combustion chemistry taking place within a front-end reaction furnace is probably more completely illustrated by the sequence of chemical reactions presented in Table VII-1. The complexity of these processes in no way invalidates the general statements contained in equations (1) through (4). Many of the species shown in Table VII-1



# SOME FURNACE REACTIONS





are short lived intermediates which probably never emerge from the front-end reaction furnace, but are nonetheless essential parts of the overall front-end reaction furnace chemistry. The reactions in Table VII-1 also give a clear indication of where hydrogen and sulphur trioxide can be produced in the overall system.

While much is known about the chemistry of the reactions shown in Table VII-1 the bulk of the work has been done under conditions that bear little relationship to the high temperature and high flow rates characteristic of a front-end reaction furnace. The kinetics of most of the processes depicted in Table VII-1 have been studied at temperatures well below the 1700-2200 degree Fahrenheit characteristic of the front-end furnace. Relatively little is known about the effect of such materials as  $\text{CS}_2$ , COS,  $\text{CO}_2$ , amines, ammonia and hydrocarbons on these reactions. All of these species are commonly found in the sour gas feed stream of sulphur plants. Carbon disulphide and carbonyl sulphide are also formed in the front-end reaction furnace primarily from the small hydrocarbon carry over from the amine stripper immediately upstream of the furnace.  $\text{CS}_2$  and COS are both important and troublesome components in the sulphur plant tail gas. Many tail gas clean-up processes currently being recommended for use do not remove  $\text{CS}_2$  and COS and thus the lower limit of clean-up using these processes cannot be below the concentration level of  $\text{CS}_2$  and COS in the tail gas. The control of COS and  $\text{CS}_2$  formation in the reaction furnace is therefore of very considerable importance as illustrated in Figure VII-2.

During the past two years the industry in Alberta has mounted a special research effort to examine a whole







### FORMATION



### DECOMPOSITION

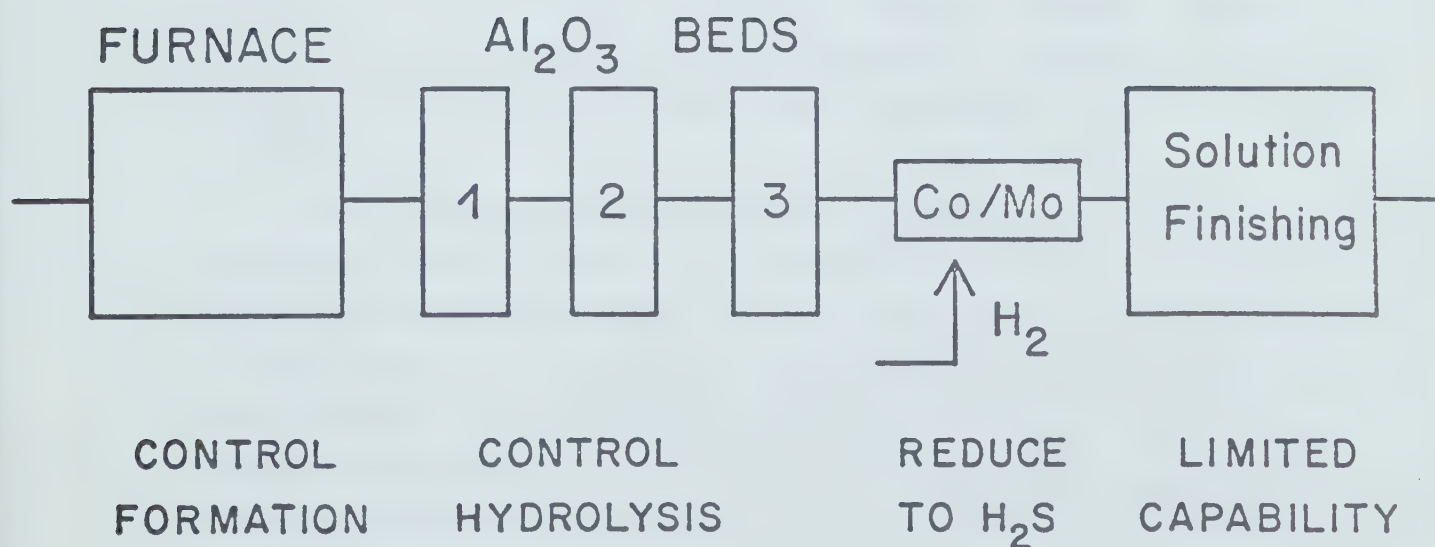


Figure VII - 2



new range of factors considered to be of importance in determining front-end reaction furnace performance.<sup>(3)</sup>

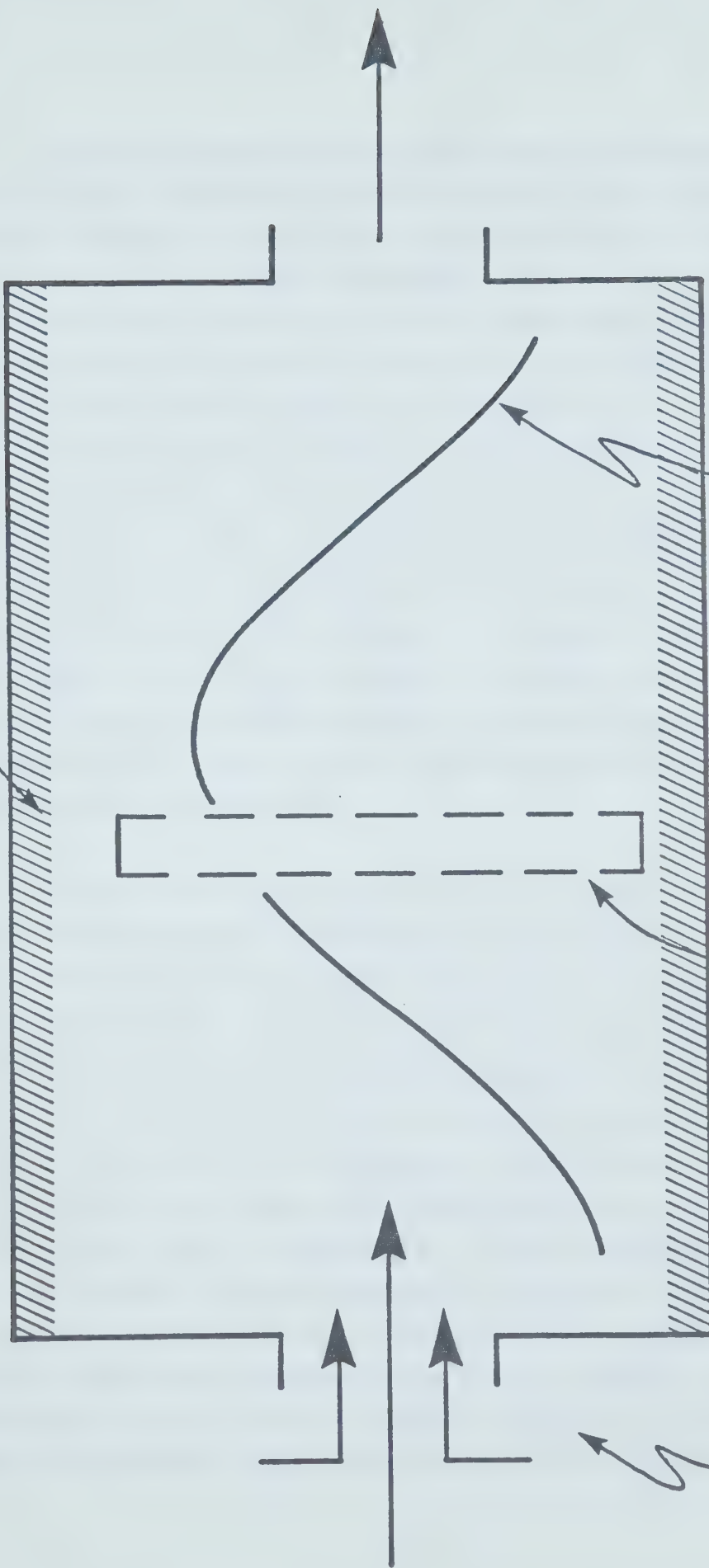
Some of the more critical elements of this study are summarized graphically in Figure VII-3. Of obvious importance in any chemical reaction is the efficiency with which the components are mixed. Considering the enormous volumes of gas fed through the reaction furnaces and the velocity that must be maintained, mixing is not as simple a matter as it might at first appear. Injection nozzle design has been and is still a primary aspect of industry's current research effort. A number of major operators, in collaboration with plant engineering companies, have continued to experiment with new techniques for achieving better mixing of the furnace feed streams. The traditional concentric axial flow nozzle design has been modified to include various forms of baffles, vanes and deflecting plugs all directed toward improved mixing efficiency within the combustion zone of the furnace. The effect of varying relative velocities of the fuel and air feeds to the furnace have been examined and tangential injection rather than axial feed of the air supply has been investigated. Vortex type burners and multiple injection ports of various designs are also being examined.

All of these variations in fuel/air injection techniques must be such as to maintain the critical  $\text{H}_2\text{S}/\text{SO}_2$  ratio required downstream in the Claus catalytic section of the plant. As a result of these preliminary tests the industry and the furnace designers and manufacturers are becoming increasingly aware of the importance of the injection configuration in optimizing front-end reaction furnace performance.



# FURNACE COMPONENTS

FURNACE LINING (CATALYTIC)



NOZZLE  
DESIGN

INTERIOR  
DIMENSIONS  
AND COMPONENTS

TEMPERATURE  
PROFILE

EXIT GAS  
COMPOSITION





A major factor determining reaction furnace performance is the temperature profile within the reaction zone and the residence time of the reactants in that zone. Injection nozzle design discussed above is of considerable importance here, but the interior dimensions and components of the furnace are equally critical. In particular the industry has recently placed more emphasis on an examination of the precise role of internal baffles or so called "chequered walls" on reaction furnace efficiency<sup>(4)</sup>. It is already evident that the location of these internal components along the furnace axis has a marked effect on the relative importance of the mixing role as opposed to the effect on temperature homogeneity within the furnace. A number of plants are already making use of the results of these studies by incorporating suggested modifications in their furnace design on an experimental basis in new installations or in older units during plant turn around.

Variations and improvements in nozzle design or interior dimensions and components are primarily of value if they result in improved conversion efficiencies. This in turn is the result of closer approach to equilibrium conditions within the reaction zone. In view of the flow reactor nature of the furnace the speed at which these chemical reactions take place relative to the flow velocity of the reactants (i.e. residence time) is also crucial. The speed of these chemical reactions can be influenced by catalysts and an examination of the possible catalytic role of furnace lining materials represents a further area of current enquiry by the industry<sup>(5) (6)</sup>. Work with so-called "wall-less" reactors has clearly shown that the catalytic role of the wall material may be a significant factor in determining furnace efficiency. While such



catalytic effects on the type of reaction shown in Table VII-1 will clearly be of importance in determining sulphur conversion efficiency similar catalytic effects may also be operative in the side reactions of the type shown in Figure VII-2. Minimization of COS and CS<sub>2</sub> formation or, conversely, maximization of their decomposition by catalytic enhancement of the appropriate reaction speeds in the flowing system would be of very considerable benefit in reducing this form of sulphur content in tail gas. Also of importance is the catalytic effect on the rates of reactions producing such other "side products" as hydrogen and sulphur trioxide. The former, as will be seen later, is a valuable component of tail gas streams in some processes that require hydrogen to remove COS and CS<sub>2</sub>. The latter is the principal source of sulphation of the Claus converter bed catalyst, a phenomena which results in reduced efficiency of this down stream section of the sulphur plant system.

Perhaps one of the great challenges facing science in the 70's is the problem of putting the results of a quarter century of elegant and sophisticated fundamental research to work for the benefit of those who have, in many instances, paid a sizeable part of the cost. This comment is particularly appropriate in relation to the gas processing industry's present efforts to apply the wealth of available fundamental combustion research knowledge to the improvement of front-end reaction furnace performance. Yet bridging the gap between the availability of fundamental information and the translation into a practical manifestation in the form of improved industrial unit performance is no less difficult a task than that of acquiring the basic knowledge in the first place. The industry's responsible attitude to the need for continued improvement in its



operation is well illustrated by its ongoing research and testing of front-end reaction furnace phenomena.

### 3. Claus Catalytic Converters

#### a. General

In recent years improvements in this section of the overall sulphur plant system are generally regarded as having been the most significant. Modifications have been introduced in both the design of the catalyst beds and in the nature of the catalyst itself. Both have led to higher conversion efficiencies and longer catalyst life. The problem of catalyst sulphation and consequent loss of activity remains a major unresolved difficulty although the current twofold attack through minimizing sulphur trioxide formation in the front-end reaction furnace and change in catalyst manufacturing techniques may provide a solution.

Research investigation of the precise role of alumina based catalysts in the reaction of hydrogen sulphide with sulphur dioxide (the Claus reaction) has been active in both Alberta and elsewhere in Canada <sup>(7)(8)</sup>. These investigations and companion studies of the fundamental aspects of gas phase heterogenous catalysis in related systems are essential to the further improvement of catalysts now in plant use and the design of new catalysts with even higher activities. Until the precise nature of the  $\text{H}_2\text{S}/\text{SO}_2$  reaction at the catalyst surface is clearly understood optimization of the catalyst role will not be possible. New techniques such as total reflectance infrared spectroscopy and scanning electron microscopy have provided the





researcher with valuable new tools for the examination of surface phenomena. It is this continuing research endeavour conducted both by industry and academia that has made possible the improvements of the past decade and that will lay the foundation for further improvements in the future.

b. New Catalysts

Alumina,  $\text{Al}_2\text{O}_3$ , in various forms remains the basis of virtually all Claus catalysts. Cobalt-molybdenum based material have recently received increased attention, but usually in specialty roles within the overall Claus system. Major catalyst producers are presently in the process of introducing new generations of catalysts which, it is claimed, will provide plant operators with improved catalyst performance. One such catalyst is claimed to have markedly improved porosity with better pore homogeneity providing higher space velocity characteristics in the catalyst bed. Absorption capability for  $\text{SO}_2$  is considered to be the highest of any alumina and COS and  $\text{CS}_2$  levels in the tail gas from such beds remains low for up to six months after initial charging.

Another "new generation" alumina based catalyst is claimed to have markedly improved resistance to sulphation deactivation and does not catalyze hydrocarbon polymerisation - a major cause of catalyst carbonation deactivation. Even after full sulphation this catalyst is claimed to retain good catalytic properties for carbon disulphide and carbonyl sulphide hydrolysis - an important method of reducing the concentration of these components in the tail gas.

These developments in catalyst manufacture have not





### *Equilibrium Conversion of $H_2S$ to $S$*

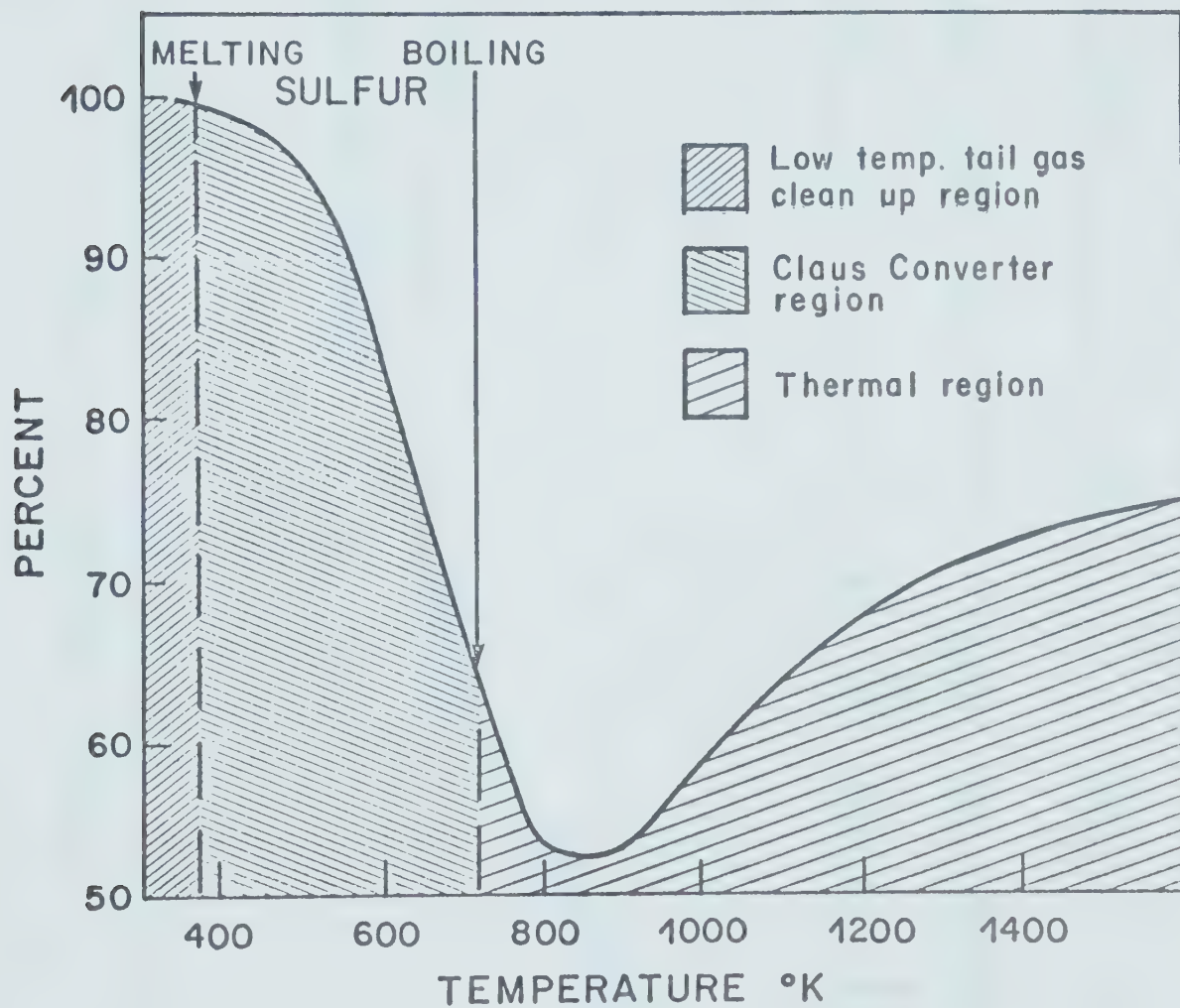


Figure VII - 4



*Sulfur Recovery vs. Ratio*

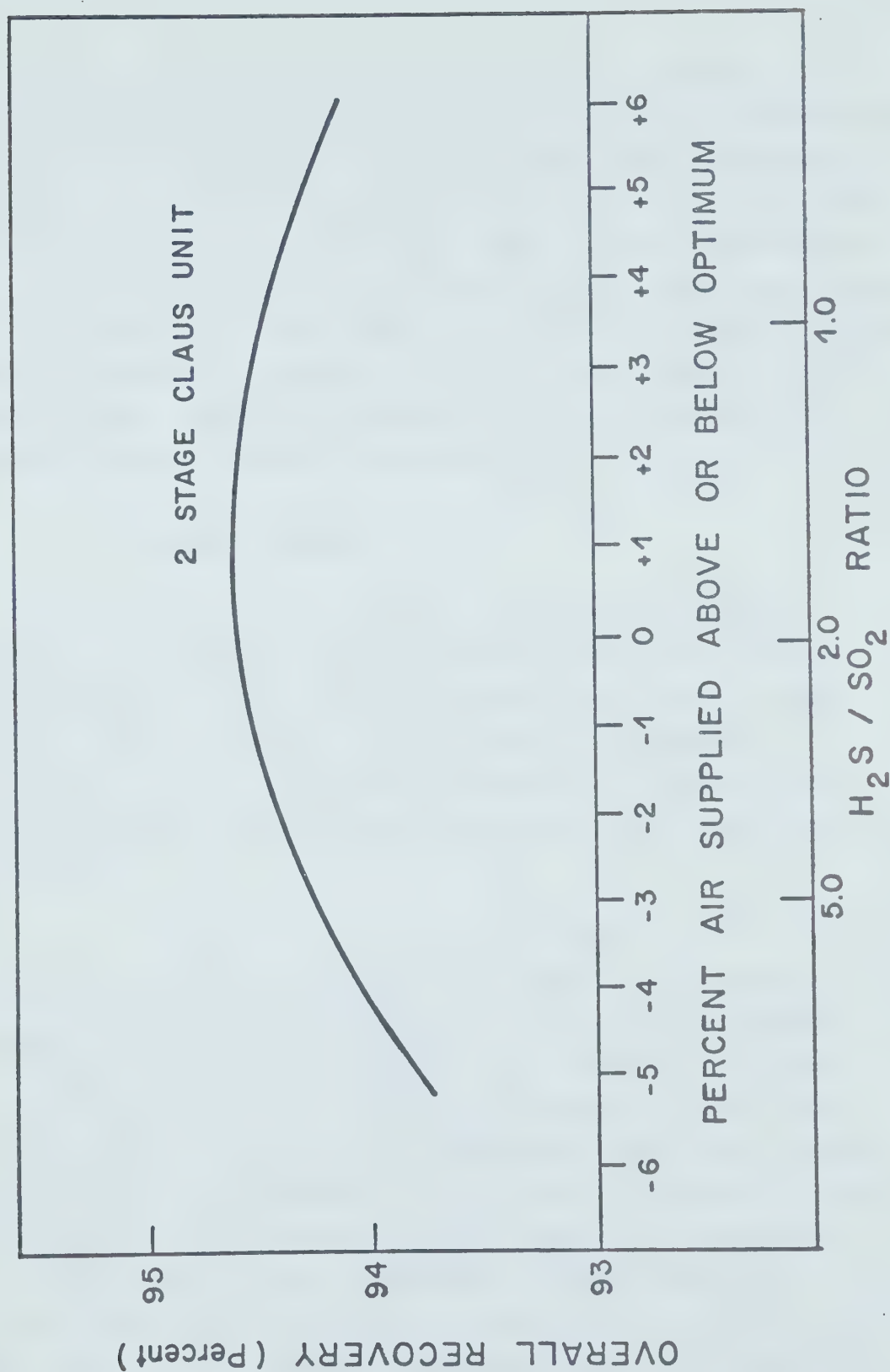


Figure VII - 5



yet had an adequate opportunity to make themselves felt in the gas processing industry. If the claims are substantiated under practical operating conditions they will represent an important and welcome contribution to the continuing effort to improve plant conversion efficiency. Such improvements, taken alone, would not be sufficient to meet the new emission level requirements. Combined with better front-end reaction furnace performance, however, they may well enable smaller plants to meet present regulations without extensive and expensive add-on tail gas clean-up units.

### c. Ratio Control

The conversion of hydrogen sulphide to sulphur proceeds not to 100% completion, but rather to an equilibrium condition where both reactants and products are present. The dependence of this overall conversion equilibrium on temperature is summarized in Figure VII-4. In the particular case of the Claus catalytic conversion equilibrium



the position attained depends on a number of factors most important of which are temperature and relative concentration of the components (Figure VII-5). The equilibrium indicated above is a very simplified version, but serves to illustrate the point to be discussed here. The problem of maintaining the optimum  $\text{H}_2\text{S}/\text{SO}_2$  ratio required for the Claus reaction has been one of the industry's principle concerns in recent years. Important though the ratio control is in the main Claus catalytic converters it becomes a crucial factor for tail gas clean-up processes that are themselves based on the Claus type reaction. Much effort has gone into the development of on-line analytical devices which continuously or intermitently determine the  $\text{H}_2\text{S}/\text{SO}_2$  ratio downstream





and feed back detected "off-balance" information to the front-end reaction furnace feed control where the ratio of  $H_2S$  to air can be adjusted to bring the downstream  $H_2S/SO_2$  ratio back to optimum. The gas processing industry has greatly increased its in-line analytical monitoring over the past few years and specially designed spectroscopic and chromatographic analytical systems have been developed. In-line analysis feeding to front-end ratio controllers has done much to improve sulphur plant operating efficiency and further sophistication of this type of feed-back optimization will undoubtedly occur in the attempt to reach higher and higher conversion efficiencies.

#### d. The Temperature Factor

As indicated in Figure VII-4, lower temperatures favour the products in the Claus reaction equilibrium. Reaction rates are slower at lower temperatures, however, requiring longer residence times or lower reactant flow rates to achieve equilibrium conditions. At lower temperatures below the sulphur dew point sulphur deposition on the catalyst becomes a serious problem and although this can be overcome by "regenerating" the catalyst bed with hot gases as is done in one currently available tail gas clean-up process, it requires multiple reactors alternately operating in service and regeneration modes. While this type of operation may be feasible for handling the low sulphur content of tail gas, it is impractical for the main upstream Claus reactors which can handle up to 50% of the total sulphur load on the plant. Apart from the need to operate at temperatures above the sulphur dew point and with reaction rates sufficiently high to permit reasonable space velocities higher temperatures in the Claus catalytic converters also favour the hydrolysis of carbonyl



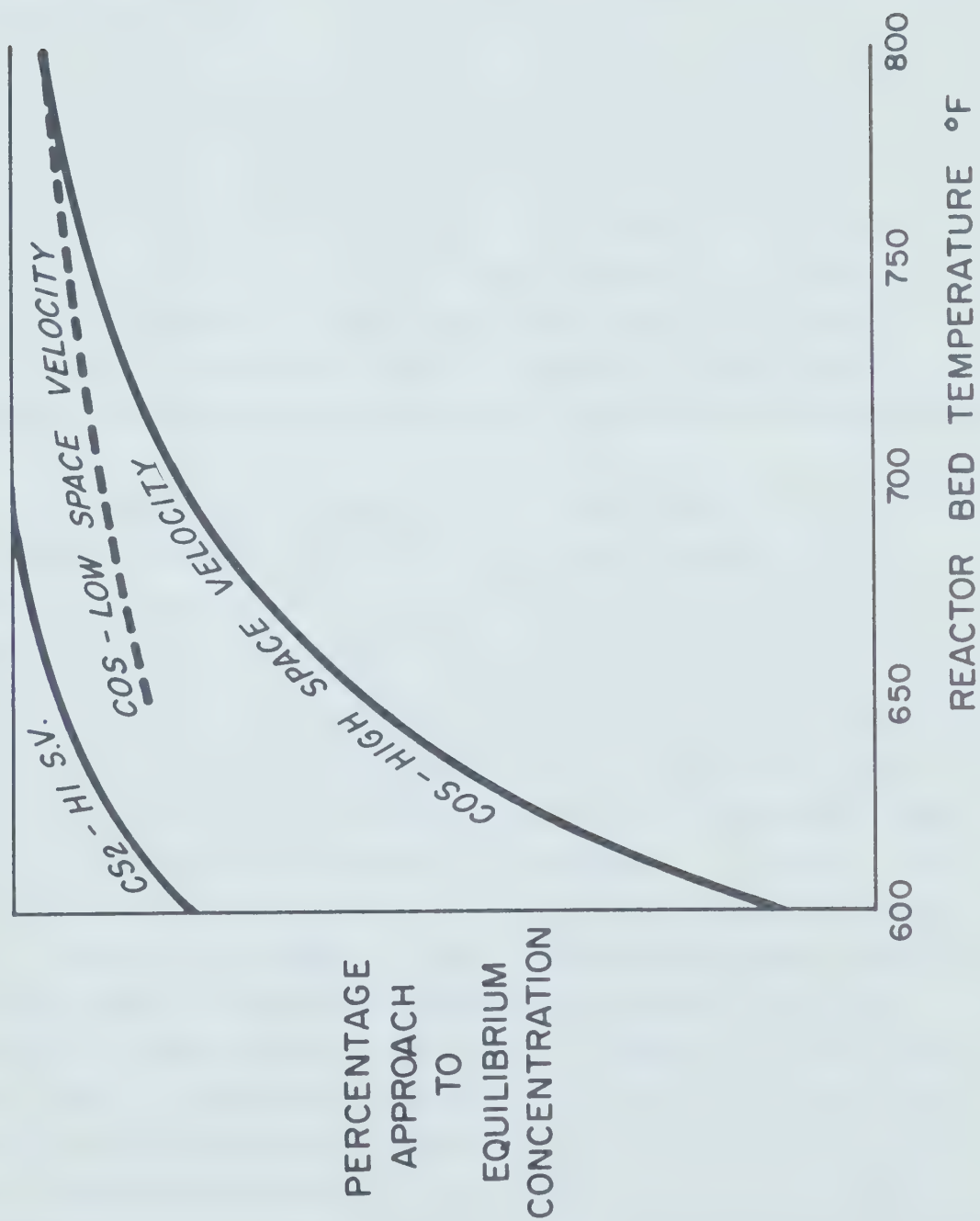
sulphide and carbon disulphide as shown in Figure VII-6/ Reduction of COS and CS<sub>2</sub> levels in the tail gas minimizes the difficult task of their removal in any tail gas clean-up process. Ironically, therefore, the plant operator faces the dilemma of "running hot" to minimize COS and CS<sub>2</sub> but thereby losing Claus conversion efficiency and increasing H<sub>2</sub>S/SO<sub>2</sub> content in the tail gas. The operating temperature problem is obviously a complex one and the final decision depends on a variety of factors many of which will be specifically characteristic of a particular plant. The knowledge and experience gained through operation of the largest concentration of Claus reactor capacity in the world has given Alberta gas processors an opportunity to lead the field in this area. Through its Associations and the trade literature the members of the industry have actively participated in exchange and coordination of this "know how" to ensure that the best methods of environmental protection are available to all those participating in the most important task of bringing Alberta's energy resources to the consumer.

#### B. TAIL GAS INCINERATION

The various factors which control the sulphur conversion efficiency in the upstream units of a typical Alberta sulphur plant have been identified. The extent to which these factors are interdependent and oft-times antagonistic to each other places a very definite upper limit on the economically practical conversion efficiency that can be achieved within the plant itself. Indeed, there are remarkably few large scale industrial process operations that consistently function at 95% efficiency or better. Yet the Alberta sour gas processor has already been required to attain and now exceed this figure. While



# HYDROLYSIS OF COS AND CS<sub>2</sub>



COURTESY PARSONS



there will undoubtedly be further improvement of the in-plant efficiency it seems highly unlikely that the larger sulphur plants can reach the required 98-99% level without further treatment of plant tail gas to desulphurize before incineration.

The capacity of the environment to receive and disperse gaseous effluents and the effects of various concentrations of these emissions on plant and animal life will be the subject of other sections of this brief. Our concern here is to examine the problem of reducing the sulphur content of Claus plant tail gas to a level which, after incineration, will yield an effluent which conforms with regulatory body restrictions on such emissions.

As indicated in Figure VII-1 the principal components in a typical tail gas are nitrogen, water vapour, carbon dioxide, hydrogen sulphide and sulphur dioxide. Minor but frequently troublesome components are carbon disulphide and carbonyl sulphide with small quantities of entrained elemental sulphur usually in the form of a fine mist. Upon incineration all sulphur containing components are converted to sulphur dioxide and it is in this form that the unrecovered sulphur in the plant system is vented to atmosphere. This is also the form in which the bulk of the sulphur emitted in coal and oil combustion occurs. Much attention has been given to the development of methods of desulphurization stack gas containing sulphur dioxide and many of these are identified in the list of patented processes included in this section. Because of the much wider market for SO<sub>2</sub> removal processes many of these techniques have enjoyed wide publicity and extensive development and testing. Re-examination of Figure VII-1, however, will reveal that the process of incineration





of a Claus plant tail gas merely compounds the important concentration problem by adding further diluents in the form of nitrogen, water vapour and carbon dioxide resulting from the combustion of the incinerator fuel. The 3% sulphur content now in the form of  $\text{SO}_2$  is more highly diluted than was the original 3% in the tail gas in the form of  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{COS}$ ,  $\text{CS}_2$  and sulphur mist.

In short the tendency has been to approach the problem of reducing sour gas processing plant sulphur emissions by developing methods of desulphurization the tail gas rather than the stack gas. Nonetheless, the enormous research and development effort being expended on stack gas desulphurization technique that will offer more attractive economics than current tail gas clean-up methods.

### C. TAIL GAS SULPHUR RECOVERY

#### 1. Methods

What are these methods for removing the last few percent sulphur from the hot, dilute effluent gas streams? As the following list of process names indicates, they are, at the very least, numerous:

Aquaclaus	Chiyoda
Beavon-Parsons	IFP
Bu Mines Citrate	Sulfreen
Calsox	Sulphoxide
Cataban	Stretford
Clean Air	Vetrocoke
	Wellman-Lord

The details of all of these processes have been extensively reviewed and no attempt is made here to examine them in detail (9) (10) (11). It is, however, pertinent to look at



those tail gas clean-up processes which have reached a stage of development that permits reasonably accurate evaluation of their applicability in the Alberta scene.

The Sulfreen and IFP methods are currently in operation at Alberta plants. The former is essentially a low temperature Claus reaction utilizing the enhanced conversion equilibrium characteristic of lower temperature (see Figure VII-4) and operating on an alternating in service/ in regeneration cycle discussed earlier. Overall conversion efficiencies in excess of 98% are claimed for a combined Claus train and Sulfreen unit. Ultimate limit of clean-up is indicated to be 2000 ppm at the stack mouth. The IFP process, unlike the Sulfreen is a solution process, but again depends on the Claus reaction between  $H_2S$  and  $SO_2$  for conversion of these gaseous components to elemental sulphur and water. Overall recoveries in excess of 99% are claimed with a combined 2-stage Claus plant and IFP solution process. Ultimate clean-up limit of the basic IFP process is comparable with Sulfreen. Neither process, however, has any inherent capability to handle COS and  $CS_2$  in tail gas, thus the lower limit of clean-up cannot be less than the  $CS_2 + COS$  sulphur values.

The U.S. Bureau of Mines Citrate process and the Molten Carbonate process were primarily developed to handle sulphur dioxide removal from smelter effluents or fossil fuel combustion stack gas. The Bumines process has many chemical similarities with the IFP, but is an aqueous solution process operating at considerably lower temperatures. The Molten Carbonate system is of interest because it gives a good indication of the kind of techniques that may be characteristic of the next generation of clean-up processes - the whole technology of molten salts as solvents



for industrial chemical reactions is in its infancy.

The Vetrocoke clean-up process is one that has been in use in Europe for some time and at least one plant in the U.S. has utilized the desulphurization technique. The process utilizes arsenic compounds and for that reason has been approached cautiously by operators concerned about the introduction of a secondary environmental contaminant in efforts to remove the primary one. More will be said later on this subject of replacing one pollutant by another!

The four remaining processes noted are all capable of reaching very low sulphur effluent levels. Two, the Beavon-Parsons and the Pritchard Cleanair, utilize the Stretford process in a common solution finishing step. Both have upstream stages where  $\text{CS}_2$  and COS are catalytically reduced to  $\text{H}_2\text{S}$  since the Stretford process - like almost all other solution finishing processes - does not convert  $\text{CS}_2$  or COS. Finally, the Wellman-Lord is not a conversion process at all, but rather a technique for reconcentrating the dilute  $\text{SO}_2$  in incinerated tail gas for refeed into the front-end of the sulphur plant. In this respect it is a process which has wide applicability beyond sulphur plant effluent treatment and indeed, many of its current applications are as a clean-up system on systems other than Claus plants.

## 2. Economic Considerations

How do these various processes compare as far as efficiency and economy are concerned? That story is summarized in graphical form in Figure VII-7. As the sulphur level decreases the cost-factor increases - exponentially! There is often a tendency to avoid or even





# HOW CLEAN for WHAT COST

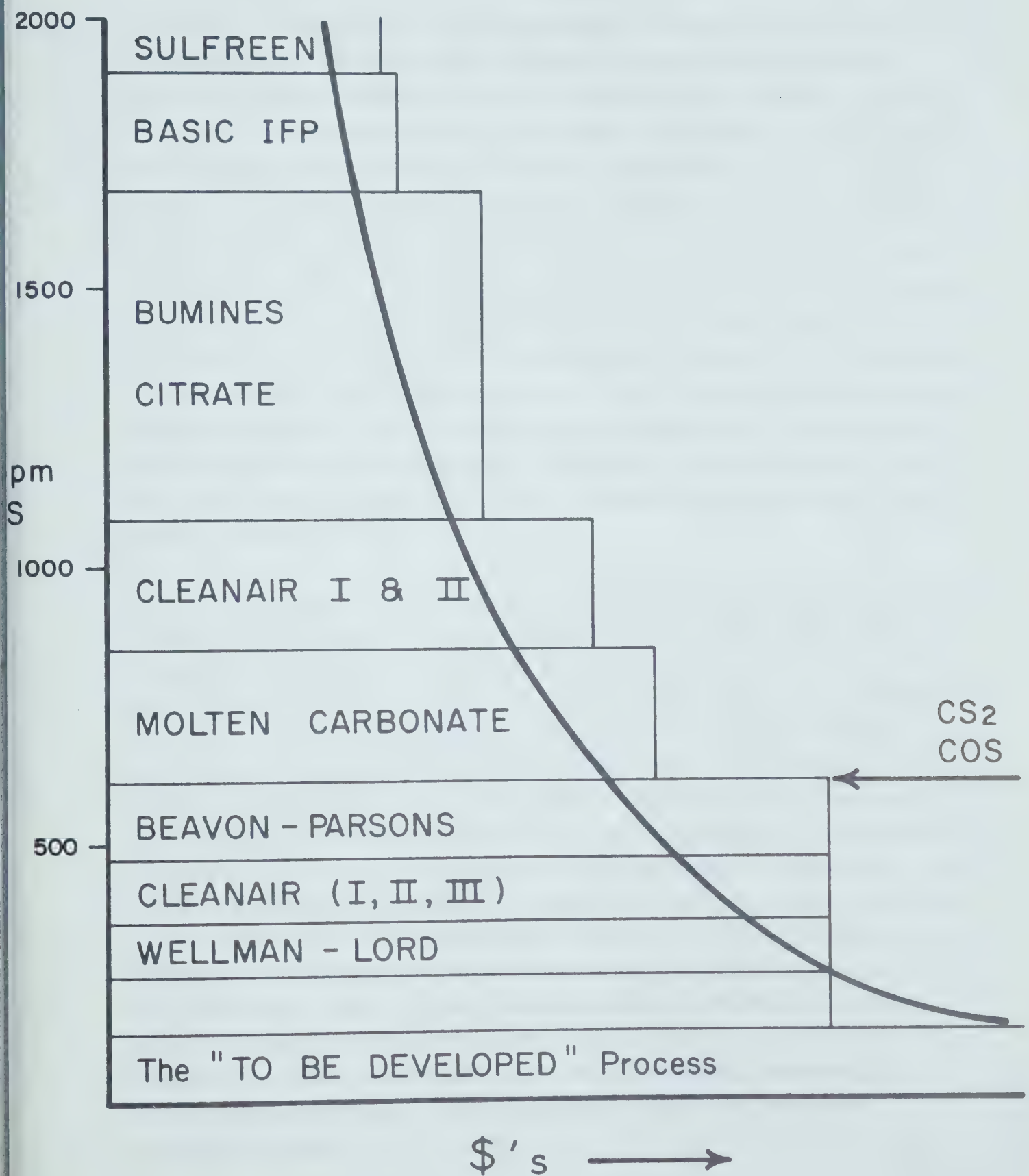


Figure VII - 7



deny the validity of cost considerations when considering environmental conservation. Those charged with bringing Alberta's vast resources to the market place, however, would be less than responsible if they were to ignore the costs of producing their product and hence establishing a fair market value<sup>(12)</sup>. The quality of the environment will only be maintained if the price to the end use consumer is kept at an acceptable level. The major influence of these cost/benefit considerations of tail gas clean-up methods will be in identifying those techniques which can be most easily and most economically incorporated into existing systems. In the long term, radical new technologies may lead to entirely different process systems, but current capital investment in sour gas processing equipment is such that for a number of years "add-on" improvements such as those discussed above will be those under consideration.

Virtually all of the clean-up processes identified in Figure VII-7 have a common feature. Their cost increases almost linearly with the load placed upon them. That is, for any given process required to attain say, 99% desulphurization, the cost of an installation to handle a 5% sulphur content tail gas stream will be approximately twice that of a 2.5% sulphur containing tail gas. This is particularly true of the solution processes where ability to handle a given sulphur loading is directly related to solution pumping capacity. This linear relationship between clean-up cost and sulphur loading is perhaps one of the greatest incentives to the industry to obtain every possible percentage point of efficiency out of the upstream units of the sulphur plant. Whether it be in the front-end reaction furnace or in the Claus catalytic converters every extra percent of conversion extracted there means that much less installed clean-up capacity of the tail gas.



Figure VII-7 also illustrates what might be regarded as a minimum cut-off for certain of the clean-up processes currently available. Rarely, under present operating procedures, does a sulphur plant in Alberta have less than 600 ppm COS and CS<sub>2</sub> in its tail gas. Accordingly, for those processes lacking the capability to convert COS and CS<sub>2</sub> this must be a lower limit. Many plants, however, have much higher CS<sub>2</sub> and COS levels in the tail gas and clearly these levels will be the limit of clean-up capability, irrespective of H<sub>2</sub>S and SO<sub>2</sub> removal efficiency of processes that do not handle COS and CS<sub>2</sub>. The capital cost for full compliance with recent regulation has been estimated at between \$30-40 million. Another figure which incorporates operating costs of tail gas clean-up units needed to meet present requirements is \$25,000 to \$35,000 per ton/day of sulphur produced by these units.

There is no doubt that enhanced sulphur recovery in the 99% range will not be economically viable. The "benefit" is environmental protection. Table VII-2 tells the story of the value of sulphur on world markets over the period in which Alberta has become a major producer. The 1970/1980 comparison of effluent production and consumption makes it abundantly clear that as we strive to reduce the level of sulphur emitted to the environment by enhanced recovery, sulphur production will continue to move ahead of consumption growth with a resulting increase in the excess of supply over demand. Development of major new large tonnage uses for sulphur, may reverse the build up of sulphur inventory, but these new uses are not yet in sight. The cost of reaching into the 99% recovery efficiency bracket must then be viewed as a direct and undiluted cost against the product of the sour gas industry that is in great demand - methane, the clean, calorific pipelineable product that more and more provides the energy





THE RISE AND FALL OF SULPHUR PRICES

<u>YEAR</u>	<u>PRODUCTION</u> <u>(TONS)</u>	<u>SALES</u> <u>(TONS)</u>	<u>SALES VALUE</u> <u>(\$000)</u>	<u>PRICE PER</u> <u>TON (\$)</u>
1971	4,500,000	2,800,000	21,000	7.50
1970	4,241,616	3,122,973	27,871	8.92
1969	3,714,120	2,619,246	60,018	22.90
1968	3,042,890	2,260,250	78,050	34.53
1967	2,168,604	2,188,645	66,557	30.40
1966	1,729,454	1,799,550	38,769	21.54
1965	1,589,586	1,818,104	25,235	13.87
1960	403,516	241,411	4,844	20.06

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demanded by those who enjoy the environment we struggle to protect.

Present requirements for clean-up do not exceed 99% or 10,000 ppm (1%) in the vented effluent. Bearing in mind the exponential cost increase with decreasing level of sulphur content in the effluent as demonstrated in Figure VII-7, some straightforward arithmetic suggests a figure of half a billion dollars may not be an unreasonable estimate of the cost of reaching 1000 ppm.

If half a billion dollars is the price of no inconvenience - and we have no assurance that even 1000 ppm effluent will provide that - would the improvement be worth the cost. What other benefits to society could be introduced for this cost? The cost, we should not forget will be borne by society directly or indirectly. Since the decision to proceed to yet lower emission limits will be made by government in the form of its regulations, government must consider its priorities and the justification for asking society to pay half a billion dollars not to remove a hazard, but to reduce an inconvenience.



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VIII COMMENTS ON ATMOSPHERIC SULPHUR DIOXIDE

Sulphur dioxide is one of the most misunderstood of the gases contained in the earth's atmosphere. On the one hand we know that sulphur is essential to life and that the greater part of our requirement is supplied from atmospheric sulphur dioxide. On the other hand we know that  $\text{SO}_2$  can be harmful and can cause severe respiratory problems, and in cases of extreme exposure can result in unconsciousness and death from suffocation. The question of whether sulphur dioxide is beneficial or detrimental hinges on the concentration of the sulphur dioxide in the environment.

It is not generally recognized that there is a sulphur dioxide cycle in the atmosphere much like the well-known carbon dioxide cycle. It is estimated by the Stanford Research Institute<sup>(1)</sup> that about 220 million tons per year of sulphur are introduced into the atmosphere, and a similar amount is removed therefrom. The chief sources are decaying organic matter, sea spray, and man-made pollutant emissions. Natural sources account for about 2/3 of the total while man accounts for about 1/3. Of the total man-made emission, 70% is estimated as resulting from coal combustion and 16% from the combustion of petroleum products, mostly residual fuel oil. The remaining amount is accounted for by petroleum refining operations and by non-ferrous smelting. Thus out of the total anthropogenic sulphur dioxide only a very small part comes from gas processing. As a point of interest, it is estimated that about 750 tons per day of sulphur are generated by the sulphur plants spread throughout Alberta, while over 3500 tons per day are emitted at one location in Ontario, i.e. Sudbury<sup>(2)</sup>. There is another significant factor in Alberta in that neither coal nor fuel oil are extensively burned in the





and these sources of  $\text{SO}_2$  are almost nonexistent here. The demands of Alberta industry on the atmosphere to absorb  $\text{SO}_2$  are comparatively small.

Sulphur dioxide, then, in low concentration is a natural and essential component of the atmosphere. What is not generally realized is the fact that vegetation, which is the source of new protein, requires nearly the same amount of sulphur as phosphorus for satisfactory growth. Plants obtain sulphur they need by direct absorption of  $\text{SO}_2$  from the air, by the absorption of sulphates which have been deposited in the soils by precipitation, and from the addition of fertilizers. Although, as previously noted, coastal areas receive sulphur from rain contaminated with ocean spray, inland continental areas are dependent on the gases in the atmosphere and man's supplementation of them. Many areas of the world are deficient in sulphur. These include 30 states in the United States, 5 Canadian provinces, and areas of Western Europe, Latin America, Australia, New Zealand and Asia. When sulphur-containing fertilizers are applied to crops deficient in sulphur, the responses are often dramatic. Crop yield increases of 1000% or more have been reported. A study of the consumption of plant nutrient in North America indicates a potential use of about 2.8 million long tons of sulphur annually in the United States and Canada<sup>(3)</sup>. Dr. D. R. Walker of the Canada Department of Agriculture Research Station at Lacombe, Alberta has examined the relationship between sulphur oxide emissions into the atmosphere and the sulphur content of Alberta soils.<sup>(4)</sup> He found that sulphur requirements for various crops were as follows:

Cereals	- 4 - 5 pounds - per acre
Legumes	- 8 -10 pounds - per acre
Grasses	- 6 - 8 pounds - per acre
Rapeseed	- 10 -20 pounds - per acre



Studies have shown that a sulphur deficiency exists in 1/2 - 2/3 of the gray wooded soils of Central and Northern Alberta. The emissions from sulphur plants in Central Alberta were examined and it was found that the annual deposition of sulphur was 2 - 4 pounds per acre. Since a portion of this is lost in surface run-off, the amount of sulphur available to plants will only be part of the total requirement. Dr. Walker concluded that "The present levels of sulphur oxides in the atmosphere in Central Alberta would seem to be contributing insufficient sulphur to the soils of the area to eliminate the sulphur deficiency that exists, except perhaps where the deficiency is marginal."

Concern is occasionally expressed regarding the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in sunlight and the subsequent combination with water to form  $\text{H}_2\text{SO}_4$  aerosols. Dr. Linzon<sup>(2)</sup> of the Ontario Department of the Environment states that the rate of photooxidation is between 0.1% and 0.2% per hour. It is more rapid where hydrocarbons and nitrogen oxides are present, which could be the case within the plume of the sulphur stacks. In any case the size of the aerosol droplet is stated by Robinson and Robbins<sup>(1)</sup> to average about 1 micron, or 1/1000 of a millimeter. These droplets are so small as to stay suspended in the air, until removed by some mechanism such as precipitation, and they are so thoroughly dispersed as to be insignificant in effect. It has been shown that even when in an experiment the droplets formed a mist so dense that visibility was reduced to 3 feet, they failed to produce injury to alfalfa and sugar beets. It has been determined that of the total mass of sulphur compounds in the atmosphere, 65% is in the aerosol form. Thus the formation of  $\text{H}_2\text{SO}_4$  aerosols is a normal atmospheric phenomenon and is not considered harmful in normal concentrations.



A study of sulphate in Alberta precipitation was made by Summers and Hitchon<sup>(5)</sup> of the Research Council of Alberta because of two observations. The first was that soil scientists had noted a decrease in the sulphur deficiency of some Alberta soils. The second was the marked reduction of hail activity in Central Alberta since 1961 and at the same time an increase in the number of reports of soft hail. The study determined that, in the summer months, a considerable fraction of the  $\text{SO}_2$  from a particular sulphur plant was oxidized and deposited as sulphate within a radius of 25 miles of the plant. However, in the winter months they state that the  $\text{SO}_2$  travels a longer distance from the source before being removed from the atmosphere. Robinson and Robbins estimate the life of sulphur dioxide in the atmosphere to be 4 days. Since the air circulates in a local concentric pattern and the systems move across the continent at a relatively slow rate of speed it is probable that there will be substantial removal of  $\text{SO}_2$  in the winter within Alberta, with additional deposition in Saskatchewan and Manitoba. The important consideration here is that in the Growing season the sulphur emissions from Alberta gas plants are deposited within Alberta and utilized by crop vegetation. The emissions are not wasted and they should contribute little to the general background level of  $\text{SO}_2$  in the world atmosphere inasmuch as they are deposited and utilized in the same general area where they are generated.

A reduction in sulphur emissions resulting from increased sulphur plant recovery requirements will actually contribute to sulphur deficiencies in the soil, at the same time increasing the sulphur which will be stockpiled and will be useless for the foreseeable future. To quote Jan Platou<sup>(3)</sup> of the Sulphur Institute of Washington, D. C., "We are thus





faced with the paradox that some of the sulphur we take out of the stack will have to be put into fertilizers to get it back into the soil, where it would have ended up if we had not taken it out of the stack in the first place."





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SULPHUR DIOXIDE

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